Various mechanisms affecting the electrical resistivity of aluminum are reviewed. Brief treatments are given of the theory, experimental techniques, and the results of experiments to measure the effect of phonons, electron–electron interactions, boundaries, vacancies and interstitials, chemical impurities, dislocations, and stacking faults on the resistivity of aluminum at room temperature and below. Also reviewed are experimental data on superconductivity, magnetoresistivity, and the effect of interactions between the various mechanisms. Where appropriate, suggested values are given for the resistivity contribution of a particular mechanism

Aluminum
1. A review of resistive mechanisms in aluminum

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We present here a brief survey of the various mechanisms which affect the resistivity of 'pure' aluminum. The presentation is limited to room temperature and below and to experiments in which a single mechanism is thought to be predominant or in which the effect of a single mechanism can be easily separated. This paper is a condensation of a much larger one which we plan to publish, in conjunction with other contributors, in monograph form in the near future. We, therefore, will welcome comments and suggestions on the content or presentation of this article.

The mechanisms surveyed are, in order of presentation: phonons, electrons, boundary surfaces, both external and internal, vacancies and interstitials, chemical impurities in the form of metallic elements, with Kondo type impurities treated separately, dislocations and stacking faults, superconductivity, magnetic fields, and the effect of interactions between mechanisms. In each case we give a brief description of the theory and of the more common experimental approaches as well as the results of various experimental measurements. Wherever possible, we suggest a value for the resistivity contribution of the mechanism under consideration. The choice of this value is based on our evaluation of the existing data. In the space available it is not possible to even present all of the data, much less write a defense of each evaluation. We claim no special clairvoyance, but offer these values in an attempt to provide a common starting point for engineering calculations and a reasonable value for the experimenter who wishes to estimate the degree to which the contribution of various mechanisms will interfere with his measurements. In all instances, the references are chosen to provide the best review of the current situation or to be representative of a particular approach. The amount of literature available is nearly overwhelming and we thus leave a complete compilation as well as the description of the evaluation techniques to the larger article mentioned above. We have prevailed upon the editors to allow inclusion of the titles of the referenced papers as we feel it may save the reader some time should he wish to pursue a given topic further.

Several abbreviations are used throughout the paper, they are: RT—room temperature, a rather ambiguous temperature usually taken to be between 295 and 300 K but the context is usually such that the ambiguity is unimportant. RRR—residual resistance ratio, generally defined in terms of resistance values as $R(RT)/R(4\cdot2 \text{ K})$ although a more puristic approach requires $[R(295 \text{ K}) - R(0 \text{ K})]/R(0 \text{ K})$. Here we assume the former definition unless it is otherwise stated. One should note however that, for aluminum, the RRR is a convenient fiction, which nonetheless represents a great improvement over chemical methods of evaluating purity, in that aluminum of only modest purity shows a slight temperature dependence of resistivity at 4·2 K and thus the ratio is not truly 'residual'. Where chemical purity is stated, we have used a 'nines' code, viz 99·998% Al = 4N8. An attempt has also been made here to give quantitative values to various adjectives used to describe high purity aluminum in the following manner:

Pure aluminum—RRR = 100–1 000

Very pure aluminum—RRR = 1 000–10 000

Ultra pure aluminum—RRR = 10 000 and up.

The highest purity aluminum yet produced has a ratio of ~45 000 and ratios near 15 000 are not at all rare.[1] However, achievement of these purities is a relatively recent accomplishment and a great many of the experiments treated here make use of pure aluminum at best.

Phonons

Knowledge of the actual resistive contribution due to phonon scattering, the so-called ideal or intrinsic resistivity, is essential to the complete understanding of the other effects to be described in this paper. Unfortunately little agreement exists, particularly in the very low temperature region where the information is most critically needed. Near room temperature where the phonon scattering is usually, but not always, the sole measureable contributor, the pure metal resistivity appears to be nearly linear with temperature although surprisingly few data exist. The ice point resistivity which is often used in conjunction with measured resistance values to derive specimen parameters, a risky procedure at best, is an evolving number. Early measurements on aluminum [2,3,4] gave

$$\rho = 2\cdot50 - 2\cdot53 \ \mu\Omega \text{ cm}$$

while more recent measurements [5,6,7,8,9,10] on, we hope, more pure specimens give

$$\rho = 2\cdot42 - 2\cdot46 \; \mu\Omega \; cm$$

We suggest

$$\rho \, (273\cdot15 \; K) = 2\cdot428 \pm 0\cdot002 \; \mu\Omega \; cm$$

represents the best value from the recent data. For other temperatures in the RT range a coefficient $a = 0\cdot0113$ $\mu\Omega \, cm \, K^{-1}$ is appropriate for pure aluminum. Another point to note on the determination of specimen parameters from the room temperature resistivity is that thermal contraction of aluminum decreases the area/length factor by $0\cdot37\%$ on cooling between RT and near 0 K.[11] This figure does not vary by more than $\pm0\cdot02\%$ (that is, $0\cdot35\%$ to $0\cdot39\%$) over a wide range of aluminum alloys.[12]

Theory. The Bloch–Grüneisen relation remains the simplest and easiest to apply of all resistivity formulas. Its construction and tables for its application are presented by Meaden [13] and others. We have constructed Figure 1 from these tables using an assumed $\theta = 400$ K, which represents a good average of the available data, and the value of $\rho \, (273$ K) given above.

More elaborate theoretical treatments exist in quantity. Generally these calculations attempt to introduce a more realistic phonon spectrum and to account for Umklapp processes, which are most likely the dominant phonon mechanism at low temperatures [14,15] and are not considered in the Bloch–Grüneisen formula. Another class of theoretical treatments attempts to use a more realistic form for the conduction electron wave functions and the actual Fermi surface shape to arrive at values for the resistivity. These calculations are described by Harrison [16] and a good description of the aluminum Fermi surface is given by Shoenberg in a recent text.[17] Agreement between calculated and experimental values of the room temperature resistivity is not generally good and variations by a factor of four are not rare.[18]

Of primary interest is the predicted variation of the resistivity with temperature. Everyone seems to agree that the resistivity is linear with temperature above room temperature, but there agreement ends. Some of the predicted possibilities for the temperature range generally below 50 K: [19,20,14]

T^5—normal phonon processes

T^4—Umklapp processes at low temperature

T^3—Umklapp processes at higher temperature

$\exp \, [-\theta/\beta T]$—Umklapp processes at very low temperatures when a minimum phonon wave vector exists for these interactions (which is most likely not the case for aluminum)

T^2—electron–electron interactions (discussed in the next section).

Between RT and 50 K a transitional behaviour is predicted. As we will see in more detail shortly, it is impossible, with the available data to make a case for any given combinations of these dependences.

Experiment. Most experiments use standard four-probe methods of resistivity measurement, although both helicon [21] and eddy current [22] techniques have been used at low temperatures. In order to avoid size effects at low temperatures with ultra pure aluminum, it is necessary to use such large specimens that voltage detection requires specialized techniques for the nanovolt to picovolt range. A number of systems exist which measure in this range using both superconducting [23] and normal components.[24] New devices employing superconducting quantum interference promise to extend the range to the femtovolt region.[25] In spite of the inconvenience of some of these techniques it seems essential that they be used for meaningful experiments as the current understanding of size effects, particularly the effect of temperature variation, is not very complete.

Finally, as the electron mean free path values increase into the millimetre region due to increasing specimen purity, more careful consideration must be given to the effect of both current and voltage contacts on the measurement.[26] This is particularly important when magnetic fields are to be applied.[27]

Results. Recent compilations [28,29,10] and bibliographies [30] which give the resistivity of aluminum exist in abundance and, in turn, reference earlier works. We have attempted to answer three basic questions here: 1. What is the behaviour of $\rho \, (T)$, particularly in the low temperature region? 2. Is the resistivity residual at 4 K for high purity aluminum? 3. How reliable are methods used to evaluate the phonon resistivity from experimental data? Briefly the answers are: 1. Unknown, 2. No, 3. Not very—but a bit more detail is in order and thus we present in Figure 2 a graphical description of the current situation regarding $\rho \, (T)$. Clearly it is impossible to give any 'correct' temperature dependence, in fact some experiments have shown that the dependence observed varies depending on the impurity types present [43] and on the defect concentration.[34] A step-like behaviour has also been reported around 4 K [38] although later experimental work has failed to confirm it.[15]
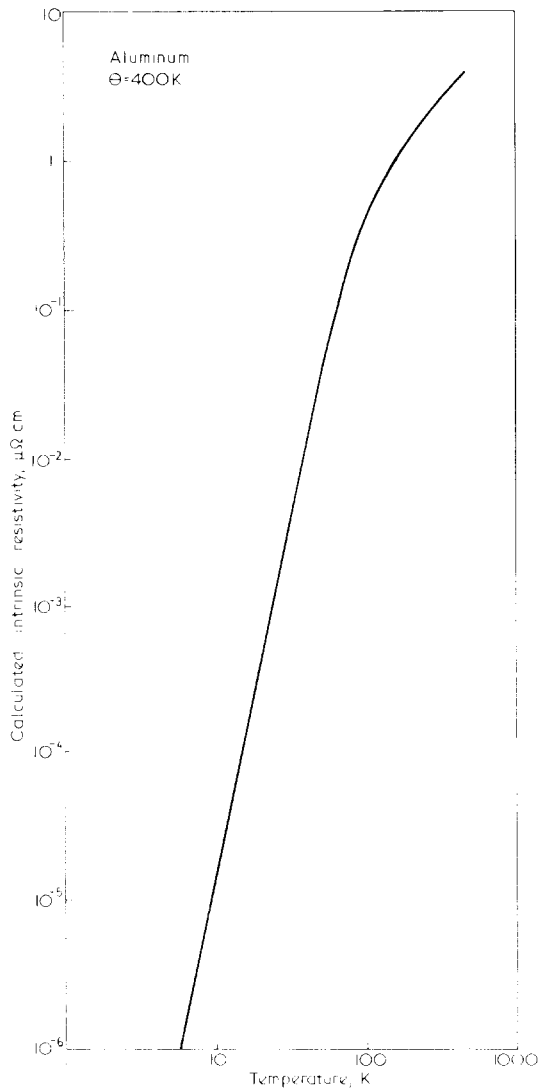
A very rough description of the situation now is that the resistivity varies roughly as T above 150 K, as T^5 around 40 K, and as T^2 or T^3 below 10 K. However a much more valuable approach to the prediction of resistivity values is to use the measured residual resistivity, $\rho \, (4$ K) is usually sufficient, and the data of Figure 1. In support of this contention we note that intrinsic resistivity data from several recent experiments [13,8,6] fall on the line of Figure 1 over a wide range of temperatures above 15 K.

The 4 K resistivity is residual to better than 1% below RRR = 1 000, the change to the residual value is 1% at RRR = 7 000 and 12% at RRR = 36 000. Note that this result rules out a strict Bloch–Grüneisen behaviour in this range as the intrinsic ratio at 4 K is $\sim10^7$ and would thus indicate an almost insignificant phonon contribution for aluminum of the highest available purity.

Electrons

Whether or not the electron–electron interaction is a significant contribution to the observed resistivity at low temperatures in high purity aluminum is still an unanswered question. It seems likely that an s–d electron scattering interaction in the transition metals is responsible for the observed quadratic temperature dependence of the resistivity at low temperatures. It is a long step to aluminum from there.

Theory. Very little theoretical work on the electron– electron interaction in aluminum exists. It is hard to justify

Figure 1. The intrinsic resistivity of aluminum calculated assuming a Bloch—Grüneisen law with θ = 400 K and ρ (273·15 K) = 2·428 $\mu\Omega$ cm. (Tabular values of the Grüneisen function taken from Meaden[13])

T, K	ρ, $\mu\Omega$ cm	ρ (273 K)/ρ (T)
300	2·722	0·892
295	2·666	0·911
273	2·428	1·00
250	2·174	1·12
200	1·613	1·50
150	1·035	2·34
100	0·4603	5·28
90	0·3545	6·85
80	0·2571	9·44
77	0·2299	10·6
50	$4·948 \times 10^{-2}$	49·1
27	$2·782 \times 10^{-3}$	$8·73 \times 10^2$
20	$6·216 \times 10^{-4}$	$3·91 \times 10^3$
10	$1·942 \times 10^{-5}$	$1·25 \times 10^5$
5	$6·070 \times 10^{-7}$	$4·00 \times 10^6$

the existence of two groups of electrons in aluminum of sufficiently different character that their interaction can relax the electron distribution to any extent. A recent paper by Hodges et al (unpublished at the time of writing this paper),[44] presents a calculation of the electron—electron interaction for a cylindrical Fermi surface which may represent a new approach.

Most theoretical work on aluminum has been devoted, then,to looking for alternative mechanisms which might

result in the observed quadratic dependence of the resistivity on temperature. Some of these are: Umklapp scattering,[18] Umklapp—impurity—electron interactions,[45,46] small angle scattering combined with size effects, and small angle scattering combined with distortions of the Fermi surface (A. B. Pippard comment [20]).

This theoretical potpourri is discussed a bit further by Chambers;[48] the general conclusion is that all reasonable mechanisms give too small a T^2 contribution and no good description of the behaviour exists yet.

Since the experimental techniques are precisely those used for the phonon resistivity we proceed to the results.

Results. Figure 2 summarizes the available data. The only experiment to look for an electron—electron term [20] does find a strong T^2 dependence and essentially no T^5 component over a wide range of temperature. Most other data in this region argue for a T^3 or a more complex fit such as a T^2 T^5 combination. Precision measurements are needed on higher purity aluminum before the questions can be answered with any certainty. Certainly one must conclude that an unusual temperature dependence exists for aluminum in the low temperature range and that existing theories are apparently inadequate to explain it.

Boundaries

The increasing applications of very pure and ultra pure aluminum to cryogenic magnet construction and the like brings the consideration of size effects very much into the realm of technology. Ultra pure aluminum conductors have electron mean free paths on the order of a millimetre and, since many conductors are of this order in size, better than half of the resistivity at low temperatures may be due to boundary scattering. Also, many new applications are being found for classical thin films, of μm size, of aluminum in deposited circuits, very low temperature thermometry, and more exotic applications using the superconducting properties of the films. Films for many of these latter uses are often very thin (<0·005 μm) and, in fact, many of their
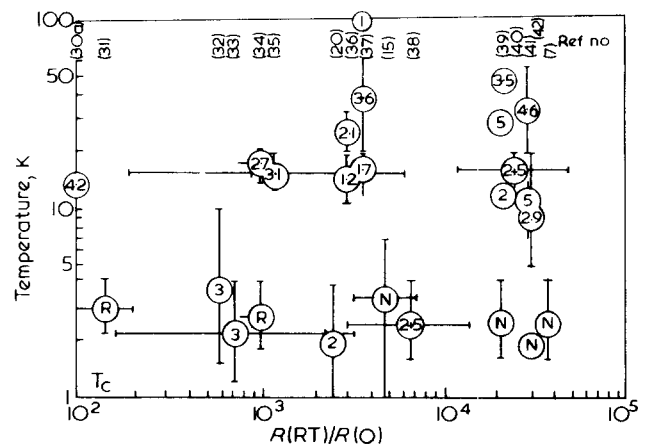

Figure 2. Temperature dependence of the resistivity of aluminum as determined by several investigators. The circled number represents the power law observed, that is, n in $\rho \propto T^n$. The symbol R indicates that the resistance measured was residual, that is, constant, N indicates that the resistance was temperature dependent but a power law was not calculated. Bars indicate the range of variables covered. Arrows are used when the range is not stated and measurements over very limited ranges have no bars. The number in parentheses at the top of the figure is the reference for all data at that RRR. T_C is the superconducting transition temperature. Note that the abscissa here is the true residual resistance ratio rather than the ratio to 4 K

desirable properties depend on the fact that the inter-
granular region consists of an oxide layer through which the
itinerant electrons tunnel.[49] The major stress here will be
on the relatively large conductors. Effects primarily of
interest to the basic physics of metals such as the r f size
effect and skipping trajectory studies are not covered here.

The internal boundary surfaces in pure metals, the grain
boundaries, have recently become of interest, again because
the increased available purity has allowed the relatively
small resistive contribution to be measured. In some instan-
ces it appears that, in fact, the grain boundary contribution
may not be as small as was previously expected. Also one
recent paper [50] describes a method of introducing quite
small grain sizes into high purity aluminum, an approach that
might be desirable as a strengthening mechanism.

Theory

Because grain boundaries in a metal unlike external sur-
faces, allow some transmission of electrons, the treatments
of the two types of surfaces both theoretically and experi-
mentally are somewhat different and we will present them
separately.

External surfaces. The general theory of d c size effects in
metals is the subject of a recent excellent review by Brandli
and Olsen [51] and an earlier one by Sondheimer.[52] Three
parameters appear, at least implicitly, in all d c size effects
theories: the ratio, $K = d/l_b$, of the characteristic specimen
dimension to the bulk electronic mean free path; the
specularity parameter, p, which is the fraction of electrons
specularly reflected from the surface; and the product ρl
for the bulk metal which should be a constant independent
of size or temperature and is given in free electron theory
by,

$$\rho_b l_b = \frac{m v_f}{e^2 n} \tag{1}$$

where n is the free electron concentration, v_f is the Fermi
velocity, and e and m are the electronic charge and mass
respectively. If one considers the real Fermi surface of a
cubic metal one arrives at a more realistic form for the con-
ductivity in terms of an integral over the surface of the
momentum-dependent mean free path,

$$\sigma = \frac{e^2}{12\pi^3\hbar} \int_{FS} l(k)\,ds \tag{2}$$

which allows for the fact that the free area of the Fermi
surface is not usually that of the free electron model and
for variations of the mean free path consistent with the
cubic symmetry of the metal. Clearly, for isotropic scat-
tering, ρl just becomes proportional to the inverse of the
free area of the Fermi surface.

Some twenty-five different theoretical treatments of d c
size effects have been reviewed. The earliest relationships,
which prove to be adequate in most instances, are due to a
suggestion of Nordheim [53] for wires

$$\frac{\rho}{\rho_b} = 1 + \frac{1}{K} \tag{3}$$

where ρ_b is the bulk resistivity and $K = d/l_b$, and the Fuchs
relationships for films,[54] which like most of its descendents
can be written simply only in the extreme limits of K. The
equations in terms of conductivity are,

$$\frac{\sigma}{\sigma_b} \simeq \frac{3}{4} K(1 - p) \ln\left(\frac{1}{K}\right) \quad K \ll 1 \tag{4}$$

$$\frac{\sigma}{\sigma_b} \simeq 1 - \frac{3}{8}(1 - p)\frac{1}{K} \quad K \gg 1 \tag{5}$$

Equations 4 and 5 are often stated with $p = 0$ which is the
most common assumption of the value of this parameter.

The later calculations, usually based on solution of the
Boltzmann equation, mostly attempt to evaluate the effect
of variation of particular parameters on the boundary
resistivity and generally give their results as a series of curves
of ρ/ρ_b versus K for different values of the particular para-
meter. The specularity parameter, p, is often treated as a
variable and in the most elaborate cases it becomes a func-
tion of the angle of incidence of the electron to the surface
as in the work of Brandli, Cotti, and Parrot.[55,56,57]
Soffer [58] considers the effect of surface roughness on p by
a statistical process. Others consider the effect of non-
spherical Fermi surfaces, Risnes and Sollien [59] making a
specific application to aluminum, the effect of an aniso-
tropic relaxation time distribution [60] and the separate
effects of small angle phonon scattering, large angle phonon
scattering and the impurity scattering interaction.[61,62,63,47]

In Figure 3 we show a qualitative comparison of several
of the theoretical approaches. The important feature from
our point of view is that above $K = 1$ nearly all theories
agree and the simple equations stated above are quite ade-
quate for corrections considering the data available for
$\rho_b l_b$. Where the purpose of the experiment is to evaluate
one or the other of the parameters discussed above, a more
careful choice of theory is in order, a task requiring nothing
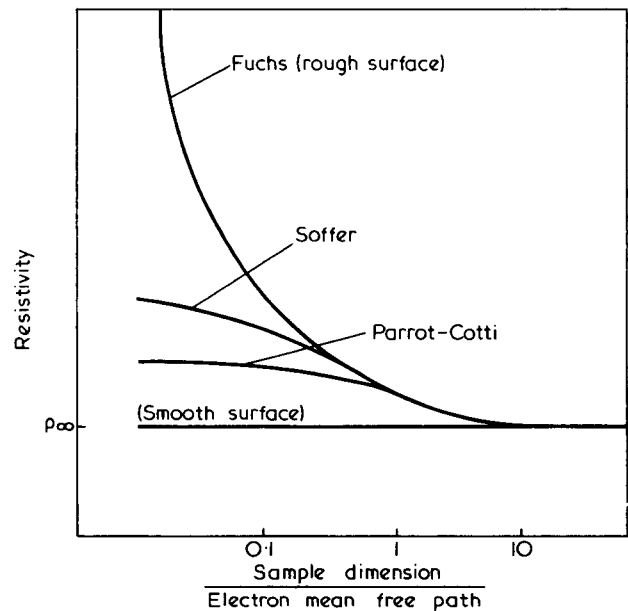short of divine inspiration.

Figure 3. Qualitative comparison of various size effect theories (from
Arp et al[1])

Grain boundaries. Some of the variability observed in thin film resistivity measurements, and to some extent in bulk measurements, is almost certainly due to the grain boundaries.[64] Theoretical treatment of the problem is much like that for external surfaces except now one needs a parameter, R, which represents the fraction of electrons scattered at the boundary. Sometimes an additional parameter, p', is also introduced to account for the specularity of the reflection.[65] A derivation similar to that leading to (2) gives,[66]

$$\rho_{gb} \equiv \frac{12\pi^3\hbar}{S_F.e^2} R \frac{S}{V} \qquad (6)$$

where S_F is the free area of the Fermi surface, or, using (2),

$$\rho_{gb} = \rho_b l_b R \frac{S}{V} \qquad (7)$$

The quantity S/V is the measure of the grain boundary area per unit volume and is not at all an easy determination to make on bulk specimens. Another treatment of the calculation [64] results in a similar expression but with R replaced by $\frac{3}{2}R/(1 - R)$. No work now exists on the actual structure of the parameter R, although some speculations are given by Schwarz and Lück.[65]

Experiment

The production of specimens small in one or two dimensions is still partially in the realm of art. The experiments discussed here use specimens whose small dimension covers the range $0\cdot1$ μm to 1 mm. Production techniques are varied, from rolling [39] and drawing to deposition in vacuum or oxygen on hot or cold substrates made of various substances [67,68,69] to photo etching,[70] chemical etching,[19] and electropolishing.[71] Most measurement schemes involve specimens covering a range of thickness and the maintenance of bulk parameters such as impurity [72,68] or dislocation content [73] becomes increasingly difficult as the size decreases.[74] The crystallinity of the films is important for two reasons: the grain boundaries themselves introduce a resistivity contribution which may be quite large as the grain size tends to be equal to the specimen thickness and, secondly it seems likely that motion of the boundaries during annealing processes can sweep impurities from the matrix.[75] One would therefore hope that both crystallite size and anneal schedule would be quoted in the experimental details of future experiments. It has also been observed that films thicker than about $0\cdot6$ μm may show a preferred grain orientation [68] which might lead to some anisotropic resistive effects due to the defect structure.

Another major problem in thin film experiments is determination of the film thickness. Some very sophisticated techniques are used, such as quartz crystal monitoring of deposition,[68] multiple beam interferometry,[69] x-ray fluorescence spectroscopy,[69] and measurement of the temperature dependence of the high temperature resistance.[76]

The actual resistance measurements are usually made by four-probe d c techniques although eddy current methods have been used which require application of a slightly modified size effect theory.[74,1] One should be cautioned against assuming a bulk value for even quite thick films at room temperature as they have been observed to exhibit

anomalously high resistivity values ($\sim$4·4 $\mu\Omega$ cm).[69] Similar caution should be observed in assuming that the resistivity is residual at 4 K for thin specimens.[39]

The production and measurement of bulk grain boundary resistivity specimens is adequately covered in the papers by Kasen [77,75] and by Andrews et al.[78]

Results

Fifteen thin film and two bulk grain boundary resistivity experiments were surveyed. In most cases, high purity zone refined aluminum was used and the experiment performed near 4 K. Results for the two types of boundaries are treated separately.

External surfaces. The experiments all measure the product $\rho_b l_b$ or a related parameter. The most outstanding feature of the results is a total lack of agreement between experiments; ρl is found to vary with purity, temperature and experimenter, usually not in any systematic fashion, and reported values for aluminum vary from $5\cdot3-13\cdot3 \times 10^{-12}$ Ω cm^2. Part of the difficulty may be the vast number of theoretical treatments available, although the great majority use the Nordheim (wires) or Fuchs (films) relationships and assume diffuse scattering in the latter ($p = 0$). As mentioned earlier, the thickness determination may involve some significant errors. In several instances a correction suggested by Dingle [79] to account for deviations from a film towards a wire, that is, for thick, not very wide strip specimens, is applied to the Fuchs theory. The measured thickness is replaced by a 'reduced' one $d_r = 2s/P$ where s is the cross-sectional area and P is the perimeter. A further contribution to the lack of agreement may be the grain boundary resistivity which is effectively thickness dependent and would cause the analysis by Fuchs' theory to give too high a ρl value. In general, polycrystalline specimens do give a higher value than single crystals, c f the experiments of Holwech and Jeppeson [39] and Risnes and Sollien,[59] independent of temperature.

The observed value of ρl increases somewhat with increasing temperature to at least 25 K. This behaviour suggests a small angle scattering effect as proposed by Olsen.[61] Magnetoresistance measurements by the author [80] in this temperature range also suggest the existence of a significant small angle contribution to the resistivity. However attempts to measure the fraction of the bulk resistivity due to small angle scattering give results varying from $0\cdot01$ [72] to 1 [81] near 15 K where the effect should be significant.

Attempts to evaluate the specularity parameter p, have almost universally met with failure, probably because a value of ρl must be assumed.[82,76]

Our evaluation of the available data suggests the following conclusions for aluminum.

1. For all but the most demanding applications, no size effect correction is necessary if $K > 10$. Roughly, this amounts to d (mm) $> 2\cdot5 \times 10^{-4}$ RRR.

2. One should not assume bulk value for the room temperature resistivity for a specimen with $d < 10$ μm.

3. The formulas of Nordheim and Fuchs (with $p = 0$) are as good as any for calculating correction terms considering the uncertainties in the parameters.

4. There is no convincing evidence now to indicate that the value of p is other than zero.

5. At 4 K the value of ρl is most likely,

$$\rho_b\, l_b = 6\cdot 0 \pm 0\cdot 5 \times 10^{-12}\ \Omega\ cm^2$$

If grain boundary effects are not specifically removed, a value of

$$\rho_b\, l_b = 9\cdot 0 \times 10^{-12}\ \Omega\ cm^2$$

is appropriate for ultra pure or very thin ($<20\ \mu m$) specimens. In the 15–30 K range, the probable value for single crystal thick films is

$$\rho_b\, l_b = 8\cdot 5 \pm 0\cdot 5 \times 10^{-12}\ \Omega\ cm^2$$

rising to

$$\rho_b\, l_b \simeq 13 \times 10^{-12}\ \Omega\ cm^2$$

for very thin polycrystalline specimens.

Grain boundaries. Only two experimental determinations of the grain boundary resistivity in bulk aluminum exist. Kasen [77] observes $1\cdot 35 \pm 0\cdot 5 \times 10^{-12}\ \Omega\ cm^2$ and Andrews et al [78] observe $2\cdot 45 \pm 0\cdot 09 \times 10^{-12}\ \Omega\ cm^2$. As outlined above, this number must be multiplied by the grain boundary area per unit volume to get the resistivity contribution and it is this determination in the inverse process which is responsible for the discrepancy between the quoted values. The determination of S/V of bulk specimens by metallurgical examination is the subject of a large amount of literature and no agreement seems to have been reached. Until more data are available one should consider an order of magnitude value of

$$\rho_{gb} \approx 10^{-6}\left(\frac{S}{V}\right)\mu\Omega\ cm;\quad \frac{S}{V}\ in\ cm^{-1} \tag{8}$$

As an idea of the magnitudes involved, Kasen reports S/V values ~ 100–$300\ cm^{-1}$ for very pure aluminum.

Several attempts have been made to determine the reflection coefficient of the grain boundaries, usually by fitting an equation like (7) or assuming a value for $\rho_b\, l_b$ and using the equation directly. By the latter technique Mayadas and Shatzkes [64] find $R = 0\cdot 17$ for the data of Andrews et al and $R = 0\cdot 15$ on their own thick film data. By a comparison of size effects and grain boundary effects in the data of Forsvoll and Holwech,[83] Schwarz and Lück [65] arrive at the figure $R = 0\cdot 5$. No value is particularly recommended.

Finally we note the observation of Andrews et al that the grain boundary resistivity is temperature dependent with ρ_{gb} (77 K) $= 1\cdot 18 \pm 0\cdot 10\ \rho_{gb}$ (4·2 K).

Vacancies and interstitials

Vacancies and interstitials fall into the general category of point defects; a third point defect, chemical impurities, is treated in the next section. Here the term interstitial is taken to mean an atom of the host lattice off a normal lattice site. Other atoms, particularly of gases, may exist in interstitial position, but essentially no data are available on their resistivity contribution. Depending on the method of production, one has vacancies alone (Schottky defects) or vacancy–interstitial pairs (Frenkel defects). The former are found primarily in quenched specimens and the latter in irradiated specimens. Except for occasional passing

reference, most information here is on vacancies alone. Direct determination of interstitial concentration is not possible, although there are some recent methods of estimating the density in low temperature irradiation measurements, and also there is no way to retain these defects which anneal out at very low temperatures.

Both theory, and to a lesser degree, experiment [84] indicate that the vacancy resistivity, not too surprisingly, is dependent on the metal in which the vacancy finds itself.

Theory. Most early calculations of the vacancy resistivity were made for monovalent metals and considered the vacancy essentially as impurity atom of valence zero to which Linde's rule could be applied as described in the section on impurity resistivity.[85] Later calculations for both vacancies and interstitials introduce the strain field of the defect although the relative effect of the field viz a viz the 'core' of the defect is still a matter for debate. The details are given by Blatt [18] and Ziman.[86]

Recent theoretical approaches frequently include specific calculations for aluminum as one of the simplest of the polyvalent metals. Harrison [16] presents a very thorough general analysis accounting for effects due to band structure, defect concentration, and lattice distortion. His single vacancy calculation for aluminum, which neglects lattice distortions results in a rather low value of $0\cdot 8\ \mu\Omega$ cm per at %. A series of OPW calculations by Fukai [87,88] taking specific account of the aluminum Fermi surface and of lattice strain gives results of $1\cdot 6$–$1\cdot 9\ \mu\Omega$ cm per at % for the first calculation and $1\cdot 06\ \mu\Omega$ cm per at % for the later one. He also suggests that an apparent temperature dependence exists for the vacancy resistivity between 77 K and 20–4 K. Finally, Reale [89] presents a semiclassical calculation which formally treats aluminum as a monovalent metal with large effective mass electrons to find $\rho_v = 3\cdot 35\ \mu\Omega$ cm per at %.

Experiment. The basic problem for the experimenter is simply to acquire a specimen with a known number of vacancies, and there the trouble starts. The usual procedure assumes that the relative vacancy concentration at any temperature is given by [90]

$$C = \exp\left(\frac{s}{k}\right)\exp\left(-\frac{E_f}{kT}\right) \tag{9}$$

where s is the formation entropy and E_f is the energy of formation of a vacancy, around $0\cdot 78$ eV. It is possible to actually measure the vacancy concentration by an elaborate scheme in which an x-ray lattice parameter measurement at high temperature is combined with a length change measurement. This procedure is described in detail for measurements on aluminum by Simmons and Balluffi [91] with the result $s/k = 2\cdot 4$. Clearly, then, the resistivity contribution of the equilibrium vacancy concentration will be

$$\Delta\rho = A\exp\left(-\frac{E_f}{kT}\right) \tag{10}$$

and one has only to quench in a vacancy concentration determined by the quench temperature and measure $\Delta\rho$.

The experiments designed to look at the vacancy resistivity quench rapidly, usually to a low temperature, often as low as 4 K but usually 77 K or room temperature and measure the resistivity change with respect to a dummy speci-

men which has not undergone the thermal cycling. Some problems exist; the quench must be rapid in order to avoid losses, an air cool of a specimen, for example, eliminates all vacancy resistivities at room temperature [92] and vacancies anneal out of high purity aluminum quite rapidly at room temperature (see the section on dislocations and stacking faults); the specimen must be sufficiently small that it is rapidly cooled throughout its entire volume [93,94] and yet large enough to avoid interference by size effects. One would not be surprised also to find the mechanical stresses inherent in a rapid quench introducing dislocations although experiment seems to indicate otherwise.[95] Many agglomeration and anihilation effects may also occur, the most common being the formation of di- or tri-vacancies or even voids [96,97,98] or the binding of vacancies to impurity atoms.[99]

Results. Experiments measuring specifically the vacancy resistivity are not numerous although many exist on the measurement of the formation energy and on irradiation or deformation recovery which could possibly give some information. Only experiments in the first category were surveyed.

One should note in passing that the resistivity of one vacancy is a term which has no meaning and ρ_v must be stated as 'per at %' or some similar relative measure of concentration. Typical vacancy concentrations used in these experiments (quench temperatures around 600 C) are ~0·1 – 0·01 at %.

The available data suggest a value for aluminum of

$$\rho_v = 2 \cdot 6 \pm 0 \cdot 5 \ \mu\Omega \ \text{cm per at } \%$$

There is no experimental indication of dependence of this value either on temperature of measurement or on specimen purity in the high purity region. For less dilute alloys, both the number of vacancies and their resistive contribution are affected by the solute.

The resistive contribution of interstitials in aluminum is much less certain but the data indicate a value perhaps half that of vacancies.

Chemical impurities

In the past most of the low temperature resistivity of metals could be easily said to result from chemical impurities. This situation is no longer necessarily the case, but chemical impurities are certainly one of the major contributors and one which the user is almost powerless to change to any degree. We present here the available information on the effect of foreign atoms in solid solution in aluminum on the resistivity. The information is derived from some twenty original experiments. These experiments are the source of most of the data in the numerous available listings, some thirteen of which were surveyed here. In a number of instances the only available source of data was a listing, the original reference being unobtainable.

In most cases impurity levels are quite low, usually on the order of hundredths of an atomic percent, and thus the impurity atoms are in solid solution in the aluminum. Our development is restricted to these dilute alloys.

For zone refined aluminum with 'natural' impurities one can use the rule of thumb [100] that one p p m impurity contributes $\Delta\rho = 0 \cdot 6 \times 10^{-3} \ \mu\Omega$ cm, that is 1 p p m gives RRR ~ 4 000, for a rough estimate.

Theory. In the space available it would be impossible to do justice to the existing theoretical developments. They divide very nicely into two groups, the early phenomonological developments and the more recent theories which derive the resistive contribution of the impurity from a scattering calculation in which an attempt is made to find a suitable model for the core potential and, frequently, for the lattice distortion and other, more subtle, effects. Complete descriptions of all techniques are given in many modern texts [86,18,16] and the earlier works are referenced there also.

Of the phenomonological treatments, two 'rules' are of primary interest in dealing with dilute alloys. Matthiessen's rule states that each mechanism contributes independently,

$$\rho_{total} = \rho(T) + \rho_{impurity} \tag{11}$$

where $\rho_{impurity}$ is a sum of contributions from each of the impurity types. Another statement of the rule is that $d\rho/dT$ is independent of impurity type or concentration. The rule is often quite serviceable as a first approximation although it fails consistently in detail; not bad, however, for an 1862 development on dirty alloys at room temperature. The second 'rule' is due to Linde and relates the residual resistivity to the solvent – solute valence difference ΔZ by,

$$\Delta\rho = a + b\Delta Z^2 \tag{12}$$

A more recent form suggested by Robinson and Dorn [101] for aluminum alloys is,

$$\Delta\rho = c(k_2 + k_1 \Delta Z^2) \tag{13}$$

where c is the solute concentration (atomic) and k_1 and k_2 are constants for solutes from a given period. They find their best results if $Z_{A1} = 2 \cdot 5$. Lucke [102] has shown that an additional term in ΔZ will allow a good fit to the data and maintain $Z_{A1} = 3$. Again, Linde's rule is often a useful approximation. Both rules tend to suffer severe failure when transition metal solutes are present.

The potential scattering calculations usually result in an underestimate of the resistive contribution. The basic problem, of course, is to calculate the scattering cross-section of the impurity atom taking proper account of screening and other interactions. The usual technique involves a partial wave calculation with the phase shifts usually determined approximately from the pseudopotential form factors.[103] The Friedel sum rule is usually taken as the expression of charge neutrality. Most calculations tend to be made for monovalent metals but some applications to aluminum exist.[104] Calculations accounting for the particular Fermi surface of aluminum by the use of multiple OPW wave functions near the zone boundaries have been made [105] which show good agreement with some data. The same paper derives a relaxation time anisotropy over the Fermi surface of ~50% for Al–Mg and ~16% for Al–Si. On the other hand de Hass–van Alphen measurements suggest that alloy scattering is isotropic for aluminum.[106]

Special techniques are generally employed in treating transition metal solutes and they will be mentioned briefly in the next section.

Experiment. Many of the experimental problems with dilute alloys are similar to those encountered in the first section. However, specimen preparation and analysis play a

most critical role here. With the exception of very dilute (p p m range) alloys, the solute concentration in the specimens is much higher than the room temperature solubility and thus the specimens are in a metastable state. Most experiments use a group of specimens covering a range of solute concentration, an approach which eliminates many sources of systematic errors. These specimens are usually prepared from a master alloy, characterization becoming increasingly critical as the purity increases.[107]

Homogenization and anneal schedules are critical, as several experiments have shown.[108,97] Anneal at 300 C seems to be sufficient for very pure aluminum but dilute alloys require 400–600 C for reproducible results. Air anneal is usually used although some solutes may be lost or depleted by this process.[109,110] Anneal times are generally long, of the order of at least hours, although one group [42] suggests that times of the order of a few minutes produce better specimens. Some effects which may occur during anneal to complicate matters are: solute clustering even at low concentrations,[111,112] solute migration to grain boundaries [1] or other defect structures, and the sweeping of solute from the matrix by growing grain boundaries.[75]

Cooling to room temperature carried out rapidly enough to prevent precipitation of the solute invariably results in some defect concentration, mostly vacancies if the stresses are not too severe. These will anneal out of high purity aluminum at room temperature, but it seems that at least four or five days are required and some solute precipitation may occur during this time. If the measurement is to be made below room temperature, a slow cool, the same for all specimens, is desirable.

One operation can save the experiment from any number of gremlins which appear during the high temperature phase: a complete analysis of the experimental specimens both for composition and for homogeneity. All of the standard techniques are useful, a very thorough characterization for aluminum is described by Shepherd and Gordon [106] for dilute alloys. The common impurities in high purity aluminum are shown in Table 1 as well as the maximum solubility for all metallic elements which have been measured.

Once again it seems that, until deviations from Matthiesson's rule are better understood, measurements need to be made in the residual region, which may be somewhat below
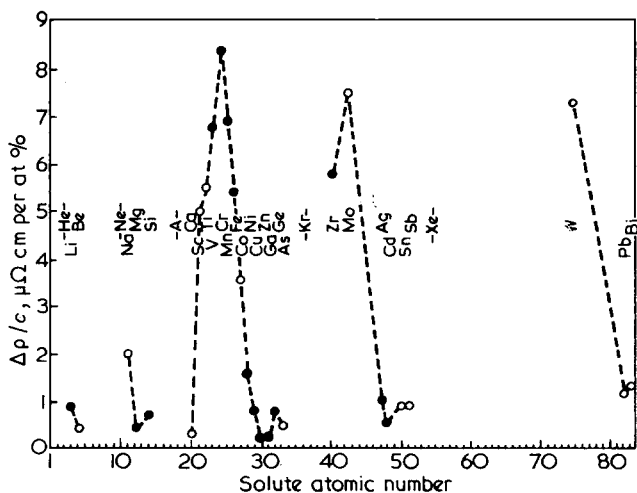
4 K for some very dilute alloys. Also here we make another plea for a room temperature or ice point measurement of the resistivity.

Finally, in Table 1 we have included data on density change and atomic size which may be useful for specialized reductions of measured data.

Results. Table 1 and Figure 4 present the available data on solute resistivities in aluminum. A quick perusal of the table should convince one that a vast amount of reliable data does not exist. Not many general statements can be made regarding solute resistivity but there are a few. For dilute alloys, the resistivity change is a linear function of solute concentration. The addition of any metallic solute to aluminum increases the resistivity. Solubility experiments indicate that impurity atoms out of solution but near the solubility limit present a lower resistivity than they do in solution by nearly an order of magnitude.[28]

The majority of the experiments surveyed here are not the type wherein one could detect small deviations from Matthiessen's rule, very few actual resistivity measurements are made. Within the rather low accuracy of the data, no dependence of $\Delta\rho/c$ on temperature is seen.

Kondo

Here we consider work on the transition elements as impurities in aluminum. These experiments are treated separately from the others on chemical impurities because they are looking specifically for the resistive minimum, indicative of local moment formation, which is seen in many other solvent metals. Thus these experiments cover a range of temperatures, usually near 4 K.

Theory. Early theory and a summary of experimental data for all metals is given by Van den Berg.[118] Major modern theoretical approaches and much experimental data are described by Daybell and Steyert.[119] Briefly, if a low temperature quasi-bound state and the associated local moment exist for the host electrons due to the magnetic impurity, then the state will break up at some higher characteristic temperatures, T_K, with a resultant drop in the impurity resistivity. Because of the increasing phonon contribution this phenomonon usually appears as a minimum in the low temperature resistivity. However, unlike most characteristic temperatures, T_K may vary over five orders of magnitude depending on the solute and solvent metals. Detailed theoretical treatment of aluminum with solutes from the transition elements of the first long period [120] indicate that no Kondo minimum should be observed. A resonant scattering partial wave calculation [121] has had limited success in deriving the large resistive contribution of these elements. Finally, a recent calculation considering the effect of an energy dependent relaxation time [122] predicts a significant variation in the resistivity of the 'nearly local moment' alloys Al–Mn and Al–Cr; the predicted changes unfortunately tend to be very small in the low temperature region where their measurement would be relatively unambiguous.

Experiment. Experimental techniques are similar to those of the last section. A set of well-characterized specimens covering a range of solute concentration is essential for the reasons mentioned earlier as well as to show up impurity–impurity interactions if such exist. The base aluminum should also be chosen with special care as a number of natural impurities are transition elements.

Figure 4. Variation of $\Delta\rho/c$ for metallic solutes in aluminum across the periodic table. Open circles indicate relatively uncertain data

Table 1. Properties of elemental metallic solutes in aluminum

(1) E	(2) NO	(3) $\dfrac{AW\,E}{AW\,Al}$	(4) Z	(5) $\dfrac{r_E}{r_{Al}}$	(6) Sol, at %	(7) Δ density, % per 0·1 wt % E	(8) Δρ, μΩ cm per at % E
Ag		4·0	1	1·01	24		1·0
As		2·8	−3, 3, <u>5</u>				(0·5)
Au		7·3	1	1·01	0·10		
Be		0·67	2	0·788	0·17	−0·04	(0·4)
Bi		7·7	3, 4, <u>5</u>	1·29	<0·02	+0·07	(1·3)
Ca	3	1·5	2	1·38	0·4		(0·3)*
Cd		4·2	2	1·09	0·14		0·57†
Co		2·2	2, 3	0·875	<0·01		(3.6)
Cr	3	1·9	2, 3, 6	0·984	0·38	+0·06	8·4
Cu	1	2·4	<u>1</u>, 2	0·898	2·5	+0·07	0·83
Fe	1	2·1	<u>2</u>, 3	0·893	0·025	+0·07	5·4
Ga		2·6	3	1·06	9·5	+0·06	0·24†
Ge		2·7	2, 4	1·03	2·0		0·79
Hg		7·4	1, <u>2</u>	1·03			
In		4·3	3	1·16	0·04		
Li		0·26	1	1·09	14	−0·05	0·86
Mg	1	0·90	2	1·12	17		0·46
Mn	1	2·0	2, 4, 7	0·903	0·90	+0·06	6·9
Mo		3·6	6	0·980			(7·5)
Na	3	0·85	1	1·33			(2)
Nb		3·4	5	1·03	0·09		
Ni		2·1	2	0·870	0·023	+0·07	1·6†
Pb		7·7	2, <u>4</u>	1·22	<0·025	+0·08	(1·2)
Re		6·9	−1, 1−7	0·961	0·26		
Sb		4·5	−3, 3, <u>5</u>		<0·022		(0·9)
Sc	2	1·7	3	1·15			(5)
Si	1	1·0	4	0·978	1·6	−0·01	0·72
Sn		4·4	2, <u>4</u>	1·18	0·02	+0·06	(0·9)
Ta		6·7	5	1·03	0·036		
Th		8·6	4	1·26	<0·0012		
Ti	2	1·8	4	1·02	0·14	+0·04	(5·5)
V	2	1·9	2−5	0·944	0·2	+0·06	6·8†
W		6·8	<u>4</u>, 6	0·987	0·024		(7·3)
Zn	1	2·4	<u>2</u>	0·972	66	+0·06	0·23
Zr		3·4	4	1·12	0·083	+0·06	5·8†

* May be value for Ca out of solid solution, the correct value may be much higher.
† No data below room temperature.

Key: 1. E = Element. 2. NO = Natural Occurrence in high purity aluminum. 1— always, 2—frequently, 3—sometimes. 3. AW = Atomic Weight. 4. Valence, for non-transition elements with several valence states the electronic contribution to the conduction band is underlined. 5. Ratio of atomic radius of element to that of aluminum as given by Rudman.[113] 6. Solubility of element in aluminum primarily from Hansen and supplements.[114,115,116] The value listed is the maximum value given in the reference, usually determined between 600—700 C. 7. Density change per 0·1 wt % of solute taken directly from Kunkle and Willey.[117] They list a density of 2·699 g cm⁻³ for 4N aluminum. 8. The resistivity increment per atomic percent of element in aluminum from a critical evaluation of published data or from compilations (values in parenthesis) where the original source of data could not be obtained.

One should also note that it is possible to create a large degree of supersaturation of transition metal solutes in aluminum [114] and at least one group is working on such alloys in great detail.[123]

Results. The six experiments surveyed have looked specifically for a low temperature anomaly in the resistivity of aluminum with Fe, Cr, and Mn as solutes, mostly in the range 1·3–4·2 K. Five of these report a negative result, the resistivity is residual to within the experimental error which typically is 0·1%. Caplin and Rizzuto,[43] with a precision of 10^{-6} claim to see a decrease in resistivity with increasing temperature of one part in 10^5 from 1·5–4·2 K for Cr and Mn solutes. This result rests on a number of assumptions and one could easily question the interpretation but no other experiment approaches this precision.

For our purposes we may consider the resistance in the residual region as constant even with a significant concentration of transition element impurities.

Dislocations and stacking faults

This is one of the few areas where theory has easier going than experiment. A myriad of difficulties arise when one attempts to introduce and measure a fixed concentration of these defects. In fact, the possibility of a stacking fault contribution to the resistivity of f c c metals first arose because of discrepancies between theory and experiment on dislocation resistivity.[124,9] It was first thought that stacking faults were unlikely in aluminum due to a high formation energy [125] but this has not proved to be the case, in fact one of the problems in quench experiments is separation of the resistivity contributions from the two types of defects. The problems are outlined in more detail below and the evaluation of some fifteen experiments, four of which specifically attempt to measure the stacking fault resistivity leads one to conclude that the numbers are still in the order of magnitude category.

The units of dislocations density are lines per cm^2 and of stacking fault density cm^2 per $cm^3 = cm^{-1}$, that is, the same as for grain boundaries.

Theory. The theoretical calculations for these extended defects are a geometer's delight. The theory of scattering by both stacking faults and dislocations is reviewed briefly by Gregory et al [126] and is discussed in several texts in detail.[86,84] A lengthy general stacking fault calculation is presented by Seeger and Statz [127] with some similarities to the grain boundary calculations such as the introduction of a reflection coefficient. The application of dislocation scattering calculations to aluminum is outlined by Cotterill.[128] The problem even when the defects are considered separately, is the evaluation of what fraction of the resistivity is due to the core of the defect and what fraction is due to the strain field. Very little agreement is seen here between authors. When the more realistic case of combined defects is considered such as dislocation loops containing stacking faults, the relative contribution of each defect type becomes a matter for debate, again with little agreement. It does seem that when very large numbers of defects are introduced such as in dislocation tangles, the contribution per unit defect will decrease.

One point on which all theories agree is that the scattering from these defects is anisotropic [129] and has at least some component which gives small angle scattering.[130] Thus it is almost certain that the resistivity contribution

will be temperature dependent [131] and this, indeed, appears to be the case.

A further impediment to the theory–experiment correlation is the refusal of the defects to occur in the same form from one experiment to the next. Linear dislocations and dislocation loops containing stacking faults are most common.[132] The stacking faults may, however, occur as three-dimensional defects such as multilayers or, at least in copper, as tetrahedra.[133] Special conditions may also produce loop free aluminum with helical dislocations [134] or other configurations.[98]

A general conclusion is that the best available theoretical calculations agree with experiment to within an order of magnitude.

Experiment. Quenching and deformation are both used to introduce dislocations into aluminum, the former technique gives a stacking fault concentration as well.[135] Measurements are customarily made at 77 K although observed temperature dependences argue for 4 K. Vacancies are eliminated by room temperature ageing and long times (~4 days) are apparently required after a rapid quench.[136] Single crystal experiments are rare and no attempt has been made to measure the predicted anisotropy in the resistivity contribution.

The major experimental problem is determination of the defect density. The only commonly used direct method is transmission electron microscopy of a thinned specimen. Unfortunately, the thinning process results in a loss of defects and estimates as to the fraction lost vary widely [73] but a correction for this loss is invariably applied as well as a correction to account for the fact that some loop orientations give zero contrast in the beam. Indirect calculational methods are used less frequently,[137,138] etch techniques almost never.[139] A recent experiment has attempted to investigate the relationship between surface markings and the underlying dislocation structure [140] and nondestructive x-ray techniques for simultaneous measurement of stacking fault and dislocation density are currently being developed.[141]

Quite low anneal temperatures have been observed to affect the dislocation structure of high purity aluminum. It is well documented that between 170 and 200 C loops anneal out and other dislocations become smoother [132] and effects have been reported as low as 70 C with the majority of dislocations removed at 120 C.[142] This same author notes that significant volume changes may occur on annealing of a deformed specimen (2·5% elongation results in a change on anneal equivalent to $\Delta\rho = 2·8 \times 10^{-6} \mu\Omega$ cm). Ultra pure aluminum has been observed to completely recrystallize on straining at room temperature,[141] indicating that dislocations may be removed even below 20 C.

Finally, it has been observed [137] that the dislocation density for a given strain increases with impurity concentration.

Results. The dislocation density in annealed aluminum is on the order of 10^6 lines per cm^2. The stacking fault density may be nearly zero or several hundred cm^{-1} depending on the details of the heat treatment. The resistivity of both dislocations [136] and stacking faults [143] is observed to be temperature dependent.

Reasonable values for the stacking fault resistivity, determined from very limited data are

$$\rho_{SF}(4 \text{ K}) = 3 \pm 1 \times 10^{-13} \ \Omega \ cm^2$$

and

$$\rho_{SF}(77 \text{ K}) = 4 \pm 1 \times 10^{-13} \ \Omega \ \text{cm}^2$$

which must be multiplied by the stacking fault density to give a true resistivity.

Data on the dislocation resistivity are more numerous with values from $0.2 \times 10^{-19} \ \Omega \ \text{cm}^3$ to possibly $9 \times 10^{-19} \ \Omega \ \text{cm}^3$. A reasonable value to use is

$$\rho_d = 3 \pm 1 \times 10^{-19} \ \Omega \ \text{cm}^3$$

with the lower limit probably the best estimate at 4 K. Multiplication by the dislocation density is necessary to get a true resistivity.

Superconductivity

Superconductivity was first reported in aluminum by Keesom [144] in 1933. Recently a great deal of experimentation has been done on the superconducting properties, particularly of thin aluminum films. Most of our treatment is devoted to the bulk properties, but we attempt to provide sufficient references to the film work so that one can easily pursue it further.

The most recent, and most complete, work on general superconductivity is the two volume text edited by R. D. Parks.[145] Rosenberg [84] presents an easily readable review which is closely tied to experiment.

Theory

Two results from general superconductivity theory are important here, first the existence of a transition temperature, T_c, below which the metal is superconducting and, second, the occurrence of a critical magnetic field H_c, which destroys the superconductivity at temperatures below T_c: the usual form, and that which applies to aluminum is

$$H_c = H_0 \left[1 - \left(\frac{T}{T_c} \right)^2 \right] \tag{14}$$

For reference, Caplin and Chanin [146] give the values $T_c = 1.175$ K, $H_0 = 104.8$ Oe for bulk aluminum. Specific calculations have been made to derive the effect of the electron–phonon interaction on T_c,[14] and to treat the effect of impurities on T_c either empirically [147] or by various calculational schemes.[148,149]

Treatments of thin film superconducting properties deal with films which are thin (hundreds of Å) compared to the superconducting coherence length ($\sim 1.6 \ \mu\text{m}$). The more common theoretical treatments of the T_c variation are discussed and referenced by Babic et al [149] while very recent work on the effect of surface phonons in grain boundaries is presented by Watton [150] and by Wells et al.[151] As well as the observed variation in T_c, another interesting thin film phenomenon manifests itself in a temperature dependent 'excess conductivity' of the form

$$\sigma \propto (T - T_c)^{-1} \tag{15}$$

observed just above T_c, a region where the bulk resistivity is residual.[152] Cohen and Abeles review the early theoretical situation,[153] the major modern theory is due to Aslamov and Larkin [154] and relates the excess conductivity to thermo-

dynamic fluctuations of the order parameter. The theory predicts no effect of purity (mean free path) on the excess conductivity which is contrary to observation.[155] This is an active area of investigation both theoretically and experimentally, at this writing the most recent treatment to review the status of the field is that of Kajimura and Mikoshiba.[156]

Experiment

Experimental techniques for the observation of superconducting transition temperatures are described by White [157] and Roberts [158] and the reference therin. Temperature monitoring and control are very critical, particularly now that accuracy values on the order of one millidegree are routinely claimed and measurements are being made of the width of the transition which is around 10 mK. One should also be aware of possible supercooling effects in aluminum, both thermal [159] and magnetic.[84] Chanin et al [160] describe the experimental details of T_c measurements on bulk, dilute alloy specimens.

Thin film preparation, a field nearer art than science, is described in detail in many texts.[161,162] The only comment to be made here is that for stable properties independent of substrate and for a significant enhancement of the superconducting transition temperature, evaporation of aluminum in an oxygen atmosphere on to a room temperature substrate is the most promising approach.[153]

Results

Once again we do a division of the section, as three distinct types of experiments exist, bulk aluminum measurements in which we are mostly interested, and measurements on the transition temperature of films and on the excess conductivity.

Bulk aluminum. For practical purposes we would suggest the value $T_c = 1.18 \pm 0.01$ K for the transition temperature of aluminum. A number of experiments have reported values with much greater precision, on the order of $1-2$ mK, but their ranges fail to overlap. This is not surprising since the transition temperature is affected by impurity type and concentration. Recent work at the National Bureau of Standards on aluminum with a RRR $\simeq 16\,000$ has given a value $T_c = 1.176 \pm 0.0015$ K for this particular aluminum [159] with an observed hysteresis which varies from 0.1 to 11 mK and which is attributed to supercooling effects.

The effect of pressure on T_c has been measured [163] and T_c is found to decrease in a non-linear way to 0.687 K at 21 000 atm. From theory one would expect superconductivity to disappear at $\sim$39 000 atm but the experiment extrapolates to >500 000 atm for complete disappearance.

The observed effects of non-transition metal impurities on T_c agree with the conclusions of Chanin et al [160] derived from extensive experiments with many solutes. Somewhat paraphrased, these are: At low ($\leqslant$0.2 at %) impurity concentrations T_c decreases linearly with reciprocal mean free path, that is, with decreasing purity. At higher concentrations, still less than 1 at %, curves for impurities with valence <3 tend to flatten out while those for impurities with valence >3 start to rise again and may even give enhanced T_c values. The changes are on the order of tens of millidegrees. One recent experiment in which a copper alloy (0.85 at %) is quenched very rapidly shows an enhancement of T_c to as high as 2.3 K which is

attributed to the smaller grain size which occurs in the alloy.[149]

Transition metal solutes, on the other hand, cause T to drop rapidly [148] with T_c = 0·7 K for 0·2 at % Mn and T_c < 0·35 K for higher concentrations. Similar results were found for Fe and Cr solutes but with a smaller rate of decrease. The shape of the critical field curve has also been investigated for Mn alloys [164] and found to be given by (14) for alloys up to ~0·1 at % Mn.

Thin film T_c. Aluminum films exhibit enhanced transition temperatures compared to the bulk metal with $T_c \propto d^{-1}$, transition widths of 2–14 mK,[165] and critical fields in the Tesla range. Most experiments surveyed work with films in the thickness range 0·001–1·0 μm with grain sizes on the order of the thickness. One film at the low end of this range gave probably the record transition temperature of T_c = 3·7 K.[153] Typical values for the middle of thickness range are around T_c = 2·0 K, and at the upper limit the bulk value is observed. There is little doubt that the grain configuration is of prime importance to the enhancement but the exact mechanism is still unknown.

Both metallic and nonmetallic impurities are observed to enhance the transition temperature of quite thick films— 3·6 at % Ge, 0·2 μm films give T_c ~ 3·6 K; Al_2O_3, 0·5 μm film gives T_c = 2·5 K.[166] Also a reversible enhancement to ~1·48 K has been observed as an aluminum film deposited on mylar is strained to 4%.[167]

Normal state effects in films. Some six separate experiments have looked at the excess conductivity in aluminum films varying in thickness from 0·008 to 0·2 μm and perhaps larger. The results of Masker and Parks [152] are typical of the group. The theoretical temperature dependence is observed independent of most film parameters. The excess conductivity is strongly dependent on mean free path, low resistivity films showing a conductivity an order of magnitude larger than predicted, in contradiction to theory. Measurements on the quenching of the conductivity by a magnetic field are interpreted to indicate that a phonon contribution to the excess conductivity is unlikely.

Magnetic fields

Application of a magnetic field strongly affects the resistivity of a metal when there are anisotropic scattering mechanisms operating. These may be boundaries, small angle phonon interactions, defects in two and three dimensions, or variations of the Fermi surface of the metal from the ideal spherical shape of free electron theory, which shows no magnetoresistive effects. The field is so large that we must restrict ourselves to a limited exposition here both in terms of text and references; more complete information is available from the author.

First, a brief description of what we are not going to discuss. Many galvanomagnetic and thermogalvanomagnetic measurements have been made on aluminum which are not related directly to the resistivity, such as the Hall effect, anomalous skin effect, Righi–Leduc effect, etc and are not discussed. Similarly we have omitted refefences to a large collection of data on aluminum as conductors for specific magnets and as a stabilizing material for superconductors.

The two major areas of importance here are the bulk magnetoresistance and the effect of a magnetic field on the resistance of small specimens—magnetomorphic effects.

Theory. The theory of bulk magnetoresistance is covered in all of the newer solid state texts and an excellent review, tied to experiment, is given by Fawcett.[168] The basic problem is the determination of the form of the diagonal terms of the resistivity tensor for a particular metal in the presence of a magnetic field. In general the two configurations, field normal to current or transverse magnetoresistance, and field parallel to current or longitudinal magnetoresistance, require different treatments, the former being closely tied to the Fermi surface topology and the latter to the scattering interactions. Calculations for aluminum are given by Jones [169] and Pippard [170] and a number of·others. The Fermi surface of aluminum, an essential ingredient for most theoretical calculations, is discussed in many texts and in great detail in several papers.[171,172] The calculated magnetoresistance behaviour for aluminum is quite simple, the resistance should rise quadratically with field until the condition $\omega\tau$ ~ 5 is satisfied (ω is the cyclotron frequency, τ the relaxation time, satisfying the condition, allows electrons to make several circuits of the Fermi surface on their field induced orbits before scattering off the orbit) at which point the resistance saturates, that is, becomes field independent.

A phenomenological device known as Kohler's rule is the most common expression of the magnetoresistance

$$\frac{\Delta R}{R_o} = \frac{R(H) - R(0)}{R(0)} = f\left(\frac{H}{R_o}\right) \tag{16}$$

that is, the variation of the resistance with increasing field is affected by temperature and purity only in the combination H/R_o. Thus all the data available should fall on a single curve plotted with these coordinates. This graph, usually in log–log form is called a Kohler plot and is remarkably successful for purity values below about RRR = 1000. Corruccini [173] gives a mathematical expression and a curve for aluminum which we present as Figure 5. At higher purities, Kohler's rule is invalid and the effect of temperature variation is quite different from that of purity variation.

Size effects in magnetic fields are reviewed in detail by Brandli and Olsen.[51] That paper and, where necessary, the references therein, provide a fine introduction to the problems and to the attempts which have been made at their resolution. Many possible geometries must be treated
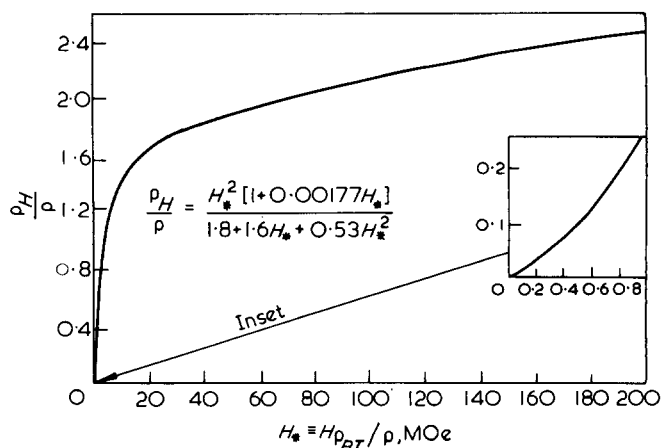

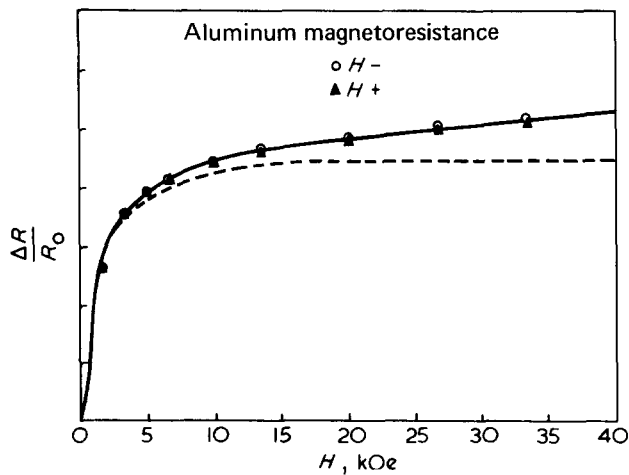Figure 5. A possible form for Kohler's rule for aluminum from Corruccini[173]

Figure 6. A typical bulk magnetoresistance curve for aluminum. Values of $\Delta R/R_0$ are discussed in the text. The dashed line results when the linear portion of the curve is subtracted off

breakdown effects may change the orbit configuration [179] for very particular field directions.

Some general comments on the magnetoresistance can be made. The slope of the linear portion is generally on the order of 0.02 ± 0.01 kOe^{-1} rising from the bottom of that range to the top as purity increases [80] but many effects seem to contribute to this behaviour and the number should be taken only as fairly representative. Transverse magnetoresistance values at 4 K vary between $\Delta R/R_0 = 1 - 3.5$ and at 20 K between $\Delta R/R_0 = 2-7$ at 40 kOe with at least one value of 10 reported. The higher values at a given temperature are found for the higher purity specimens. Longitudinal magnetoresistance measurements show similar results but the values are generally half as large. For any specimen purity $\Delta R/R_0$ rises with temperature, more rapidly the higher the purity, and appears to reach a peak value at near 15–20 K, the peak occurring at a lower temperature for the higher purity material.[80] Only limited data are available to support this conclusion, but, in any event, there is no question that Kohler's rule is not obeyed when the specimen purity exceeds RRR = 1 000.

One point which is critical for applications and which is easily missed is the following. In spite of high values of $\Delta R/R_0$, the higher the purity of aluminum the lower will be its resistivity in a field, at least at temperatures below 20 K.[180]

Several authors have suggested that measurement of the magnetoresistance may provide a technique for separating the resistive contributions of various types of defect structures[129]; most work has been on copper but at least one group has looked at aluminum with some success.[181] An experiment on the effect of transition metal impurities on the magnetoresistance of aluminum showed agreement with Kohler's rule which is contrary to the effects of these impurities in most other metals.[182]

Magnetoresistive effects measured at helium temperatures on thin specimens (generally ~0.1 mm) tend to be complicated as outlined earlier; however, experiments on films [83] and wires [183,71] do show some general behaviour patterns. In most cases the 'normal' magnetoresistance is subtracted from the data and this is usually done by assuming an extension of Kohler's rule proposed by Olsen.[61] The general behaviour for both films and wires is then a rise of $\Delta R/R$ to a maximum of about 0.5 at between 0.5 and 2 kOe and a drop to the highest field measured (2–12 kOe), in the case of some films. For certain orientations of the field, the drop reaches a minimum and then shows a Sondheimer oscillation pattern to the highest measured field. In some wires, $d < 0.09$ mm, the resistivity in the field is observed to fall below its value at zero field.[71]

separately; whether the specimen is a film or wire and the field direction with respect to the plane of the former or the axis of the latter are all important. A specific application to aluminum films has been made by Druyvesteyn,[174] using a two band model, with some success. In general, in the absence of bulk magnetoresistance, the field tends to remove the surface scattering and to return the resistivity to its bulk value although complete restoration is not predicted for most orientations. Under certain special circumstances Sondheimer oscillations in the resistivity with increasing field are observed in aluminum films [175,83] and perhaps in fine wires. The source of the oscillations is related to the interaction with the surface of the specimen by electrons on extremal orbits on the Fermi surface and is described in detail by Chambers in a recent text.[17] The effect is not usually large.

Experiment. Four probe resistivity techniques are by far the most common approach to magnetoresistance experiments. Most experiments now use static fields, usually from superconducting magnets. Attachment of both potential and current probes becomes much more critical when a magnetic field is to be applied.[176,177,27] For single crystal experiments on ultra pure materials the field orientation becomes very important and measurements on probe pairs on adjacent faces of non-cylindrical specimens are necessary.[27] Reversal of both field and current is often used to eliminate various spurious voltages such as Hall signals on misaligned potential probes.

Results. At least thirty experimental measurements of the bulk magnetoresistance of aluminum have been reported since about 1960. Almost without exception the predicted saturation of $\Delta R/R_0$ does not occur in either the transverse or longitudinal configuration, but usually a linear behaviour of rather low slope is observed at high fields both for single crystal and polycrystalline aluminum. Figure 6 is a generalized picture of the results of a typical measurement.

The single crystal measurements in which rotation diagrams of the transverse magnetoresistance were made indicate that the Fermi surface is closed, although in some instances the anisotropy is larger than one would expect from theory,[178] and it has been suggested that magnetic

Interactions

The mechanisms treated so far seldom act independently of each other and their interactions are not always well understood. In this section we will describe briefly the interactions which have been observed and several of the proposed explanations. Almost all of the available theoretical literature, and most of the experiments, concentrate on the interaction between the phonon effects and either the impurities or the external boundaries. One should note that these deviations are not necessarily small, they may be as large as 5% at room temperature and 10% or larger around 100 K.

Theory. We are considering deviations from Matthiessen's rule (11) and for this purpose we write

$$\rho(T) = \rho_i(T) + \rho_0 + \Delta(T) \tag{17}$$

where $\Delta(T)$ represents the resistive contribution from the interaction. As mentioned above, forms of Δ are derived for the case of impurities and/or of external boundaries. The developments range from mostly empirical [182,72] to quite complex calculations from the Boltzmann equation.[185,186] This seems to be another area which is positively lush with theoretical treatments and rather sparsely populated by good data. Much of the work, both experimental and theoretical, has been devoted to aluminum.

A number of interaction mechanisms have been proposed for the impurity-caused deviations and the effect of each one calculated in detail. Seth and Woods [6] discuss and reference all of those currently in contention. It seems unlikely that dilute alloys cause any change either in the phonon spectrum or the electronic structure of the metal except very locally. Effects which have been considered as possibly important are inelastic scattering by the vibrating impurity, perhaps with a modification of the impurity potential giving a phonon assisted impurity scattering and a multi-band effect in which one assumes separable and different relaxation times for the (usually) two bands. In addition, within a given band the relaxation times for phonon and for impurity scattering are also separable. Anisotropy of these relaxation times with position on the Fermi surface and, for the phonon scattering, their different variations with temperature, give deviations of the total resistivity.

Deviations are observed in thin specimens, both foils and wires, similar to those caused by impurities [72] and several theoretical treatments have been proposed.[63,47] The similarities are sufficiently good that it has been proposed that the Matthiessen's rule deviations, in aluminum at least, due to impurities and due to surfaces might have a common origin, probably in the two band theory,[187,39] but this idea is not universally accepted.[72] It has also been proposed [45] that the T^2 dependence of the resistivity observed at low temperatures may be due to deviations resulting from an impurity—Umklapp interaction.

In any event, various forms of the two band model have been quite successful in reproducing at least the general form of $\Delta(T)$ for impurity problems.[188,189] In fairness one should add that calculations of impurity oscillation and interference effects also give qualitative agreement with experiment.[190,32] It seems that the earlier conclusion of Alley and Serin [184] is still valid—there is not yet any way of deciding which of the models is nearest to the actual explanation for the observed effects, although the two-band approach currently seems to be the most promising.

Experiment. The experimental techniques are described in earlier sections for the most part but some further operations are sometimes performed in order to properly intercompare alloy and pure metal data. These involve corrections of the resistivities to the same atomic volume and corrections for variations in thermal expansion of the alloy vs the pure specimens. They are discussed by Seth and Woods [6] in some detail but are not used by them, primarily for lack of data from which to derive the correction terms. Carter and Blatt [188] apparently have applied a correction to constant volume to their data. These corrections are not often applied in the earlier literature.

Results. Early measurements of the impurity caused deviations from Mattheissen's rule by Alley and Serin [184] led them to propose the equation

$$\delta\rho = a(T)\rho_0 \tag{18}$$

where $\delta\rho = \rho_0 + \Delta$, in the terminology of (17). For aluminum they suggested the values $a(77\ K) = 1\cdot11$ and $a(273\ K) = 1\cdot12$ and these values are sometimes used to correct experimental measurements of impurity resistivity. Later results indicate that such a simple phenomonology was, as one might expect, too good to be true although it does give a useful order of magnitude value for the room temperature deviations. The observed variation when measurements are available over a wide range of temperatures is shown schematically in Figure 7. Curves which show a maximum, (a) and (b), are usually found for the noble metals as solutes,[184,32,6] there is some question whether or not these curves cross the $\Delta = 0$ axis; if they cross at all it is above $T = 200\ K$ and they cross with a low slope. Transition metal solutes usually give curves, such as (c), which show the knee and then a relatively level region [190] while Mg gives the upper curve, (d), for compositions <1 at %.[184,6] In general the magnitude of the deviations increases with solute concentration over the dilute alloy range and it has been suggested that one should plot Δ/c as the important parameter [32] but the approach has not been too successful. A few attempts have been made to fit the low temperature data to theoretically predicted curves but the results have not been particularly encouraging.

The results observed for Matthiessen's rule deviations in aluminum foils can also be described in Figure 7 if the ordinate values are decreased by an order of magnitude and the temperature values halved. The thinnest foils give the largest values, all curves apparently turn over and some probably do cross the axis near 50—60 K. Limited data are available and most of the above conclusions are drawn from Holwech and Jeppesen.[39]

Still in the category of Matthiessen's rule deviations, that is, those involving interaction with the phonon spectrum, are several observations on cold worked aluminum which indicate no deviations to within ~1% [191,192] in contradiction to the results of an earlier measurement.[193]
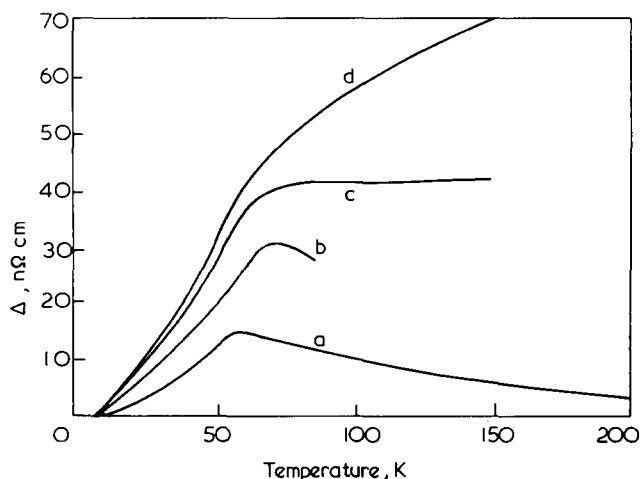

Figure 7. General behaviour of impurity induced deviations from Matthiessen's rule in aluminum for a wide range of solute metals. Which of the lettered curves is observed depends both on the solute and on its concentration as discussed in the text

As we mentioned earlier, significant deviations have been observed both for dislocations $[\rho_d(80 \text{ K})/\rho_d(4\cdot 2 \text{ K}) = 1\cdot 6]$ [136] and for stacking faults $[\rho_{SF}(300 \text{ K})/\rho_{SF}(78 \text{ K}) = 1\cdot 2]$,[143] these authors also report no deviation in the dislocation resistivity over this range.

Other interactions which can affect the resistivity are the binding of vacancies to impurities and the removal of impurities by mobile vacancies.[98] Similarly grain boundaries [77] and stacking faults [194] may remove impurities from the matrix and thereby lower their scattering effectiveness. Also dislocations interact with impurities in several ways, the value of ρ_d depends on the concentration and type of other impurities present [131] and the density of dislocations introduced by a given strain depends on the impurity content.[137] Furthermore ρ_d is observed to decrease with increasing dislocation density.[142]

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