

Measurements of the High-Temperature Electrical Resistance of Aluminum: Resistivity of Lattice Vacancies*

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The electrical resistance of a 99.995% aluminum wire was measured at temperatures from 14 to 655°C. Values of temperature coefficient of resistance and of resistivity are derived; they differ somewhat from earlier work. The resistivity values show a progressive increase above the expected values at high temperatures; this is ascribed to scattering by thermally generated point defects of the type which add atomic sites (vacancy-type defects), whose equilibrium concentrations have been measured directly in identical material at identical temperatures by Simmons and Balluffi. Three different semi-empirical methods were used to estimate the expected values of the ideal lattice resistivity in the absence of defects; they gave similar results. The limitations of extrapolation methods are discussed. The resistivity increment ascribed to the vacancy-type defects was then obtained by difference and can be represented by $\Delta\rho = (4.4 \times 10^{-3} \text{ ohm-cm}) \exp(-0.77 \text{ ev}/kT)$.

The observed formation energy is in close agreement with that obtained by direct concentration measurements and with that obtained in various quenching investigations. This increment is nearly twice the value expected from extrapolation of recent quenching work from the interval 260° to 320°C, however. This relatively small discrepancy can be ascribed to three factors, whose relative importance cannot be precisely evaluated at present. They are (1) failure of quenching techniques to retain all of the equilibrium defect concentrations, (2) the presence of appreciable divacancy concentrations at the highest temperatures, and (3) a contribution to the high temperature resistivity arising from lattice anharmonicity. The increment of about 0.30 $\mu\text{ohm-cm}$ at the melting point (660°C) corresponds to a resistivity 3 $\mu\text{ohm-cm/atom } \%$ monovacancies in agreement with a crude estimate based upon known effects of solute atoms of different valence.

I. INTRODUCTION

NOW that lattice vacancy-type defects have been identified as the predominant thermally generated defect in aluminum and that their equilibrium concentrations at different temperatures have been determined,¹ measurements of other physical properties of metals influenced by these lattice defects at these temperatures acquire renewed interest. Comparatively few well-established high-temperature data of sufficiently high accuracy have been reported. Moreover, the principal difficulty in the interpretation of such work lies in obtaining a sound estimate of the values the property measured would have in a crystal without such defects, since these values must be known in order to find the defect contribution by difference.

Thermodynamic variables such as energy content, volume, and compressibility can be considered the most fundamental in nature and therefore, in principle, the most amenable to interpretation. A number of writers have analyzed measurements of energy content²⁻⁵ and volume⁶⁻⁹ from this standpoint. The magnitude of the relative contributions by the defects

to such properties is small, however. These relative contributions can be estimated for aluminum (for a vacancy concentration near the melting point of about 10^{-3}) as about 3.5×10^{-3} increase in energy content, about 1.5 to 3×10^{-3} increase in volume (depending on the lattice relaxation around each defect), and about 2×10^{-3} decrease in elastic constants (taking the defects to be voids^{10,11}). While detailed theories exist for these variables the high-temperature region has not yet received a proportionate amount of attention. Estimates of ideal crystal properties in this region have usually been made by semiempirical extrapolation methods. Such methods may fail to take into proper account other possible effects occurring in the same temperature interval, such as lattice anharmonicity,¹² and secondary changes in the properties of the host crystal, such as localized lattice vibrational modes.¹³

Electrical resistivity, ρ , is another property of interest, and in this case, the defect contribution is relatively large. For 10^{-3} defects, the relative contribution $\Delta\rho/\rho$ is 3×10^{-2} (anticipating our results for aluminum). This is a favorable case because resistivity measurements of sufficient accuracy are easily made, and because possible errors in estimation of the ideal crystal resistivity, ρ_i , become of somewhat less relative importance.

The present paper reports measurements of electrical

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¹ R. O. Simmons and R. W. Balluffi, preceding paper [Phys. Rev. **117**, 52 (1960)].

² R. W. Christy and A. W. Lawson, J. Chem. Phys. **19**, 517 (1951).

³ L. G. Carpenter, J. Chem. Phys. **21**, 2244 (1953).

⁴ D. K. C. MacDonald, in *Report of the Conference on Defects in Crystalline Solids, Bristol, 1954* (The Physical Society, London, 1955), p. 383.

⁵ G. Borelius, Arkiv Fysik **15**, 65 (1959).

⁶ A. W. Lawson, Phys. Rev. **78**, 185 (1950).

⁷ S. D. Gertsriken, Doklady Akad. Nauk S.S.S.R. **98**, 211 (1954); S. D. Gertsriken and B. F. Clusar, Fiz. Metal. i Metalloved. Akad. Nauk S.S.S.R. Ural. Fileal **6**, 1061 (1958).

⁸ P. Jongenburger, Phys. Rev. **106**, 66 (1957).

⁹ G. Borelius, Arkiv Fysik **16**, 119 (1959).

¹⁰ F. R. N. Nabarro, Phys. Rev. **87**, 665 (1952).

¹¹ For detailed calculations on Cu and Na see G. J. Dienes, Phys. Rev. **86**, 228 (1952); **87**, 666 (1952).

¹² Examples of recent accounts are: J. N. Eastbrook, Phil. Mag. **2**, 1415, 1421 (1957), who treats energy content and volume, and D. J. Hooton, Phil. Mag. **3**, 42 (1958).

¹³ See for example K. F. Stripp and J. G. Kirkwood, J. Chem. Phys. **22**, 1579 (1954); and E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955).

TABLE I. Comparison of various measurements of electrical resistance of aluminum.

Temp. (°C)	This work	Resistance ratio $R(T)/R(20)$		Temperature coefficient $[(dR/dT)/R(20)] \times 10^3 \text{ deg}^{-1}$		
		Holborn ^{a,b}	Pochapsky ^{b,c}	This work	Taylor <i>et al.</i> ^d	Pochapsky ^e
20	1.000	1.000	1.000	$4.23 \pm 1\%$	4.29	$4.03 \pm 2\%$
100	$1.339 \pm 0.02\%$	1.326	$1.331 \pm 0.05\%$	4.26	...	4.18
200	1.766	1.736	1.756	4.28	...	4.38
300	2.200	2.156	2.206	4.39	...	4.56
400	2.648	...	2.679	4.54	...	4.78
500	3.115	...	3.174	4.83	...	5.10
550	3.364	...	3.437	5.06	...	5.34
600	3.627	...	3.710	5.40	...	5.65
625	3.764	...	3.856	5.59	...	5.86
650	3.907	...	4.008	5.84	...	6.11

^a See reference 15.^b Using $R(20)/R(0) = 1.088$ from reference 16.^c See reference 16.^d See reference 17.

resistance of high-purity aluminum *versus* temperature which were taken concurrently with the measurements of the concentration of vacancy-type defects¹ on the same specimen material at the same temperature. Accurate corrections for thermal expansion were made to obtain resistivity changes; strictly comparable defect concentrations and resistivity data were, therefore, obtained. The observed resistivity, ρ , was extended into the temperature interval where thermally generated defects were known to be present by a variety of methods, all of which produced similar results. The limitations of extrapolation methods are discussed. The derived values of $(\rho - \rho_i)$ are combined with the measured vacancy-type defect concentrations in order to (1) estimate the resistivity increment per atom percent monovacancies, (2) estimate the energy of formation of the defects, and (3) evaluate some results of various quenching experiments.

II. EXPERIMENTAL

The aluminum used¹⁴ was originally 99.995% pure with principal impurities listed as 0.003% Cu, 0.001% Si, and 0.001% Fe. It was annealed a few degrees below the melting point (660°C) for several days, the major portion used as a specimen for simultaneous length and lattice expansion measurements,¹ the remainder swaged and drawn into 0.43-mm diameter wire. The resistance ratio, $R(273^\circ\text{K})/R(4.2^\circ\text{K})$, for the wire after annealing was 414, essentially the same as for the starting material. Therefore, it is believed that the present measurements and those on equilibrium vacancy concentrations were made on identical material.

Figure 1 shows the general arrangement of the potentiometric specimen in the furnace. The gauge length was supported without strain in a homogeneous temperature environment as measured by the Pt *versus* Pt=10% Rh thermocouple which could be moved parallel to the furnace axis within the high thermal conductivity spectrographic purity graphite core.

¹⁴ The material was kindly donated by the Aluminum Company of America.

Temperatures reported here coincide exactly with those of reference 1. The specimen gauge length and current leads formed a continuous 5 m length of wire; the potential leads fabricated of the same high purity aluminum were spotwelded in place. The specimen configuration was stabilized against changes in dimensions and oxide skin thickness by heating near the melting point for several days prior to the measurements. A prepurified nitrogen atmosphere was maintained in the electrically heated furnace.

Both lack of contamination of the specimen and condition of thermal equilibrium were verified by the reversible nature of the resistance values upon heating and cooling within the present experimental error.

III. RESULTS

Figure 2 shows the measured values of electrical resistance at temperatures from 14.2 to 654.6°C compared to the resistance at 20°C. These are com-

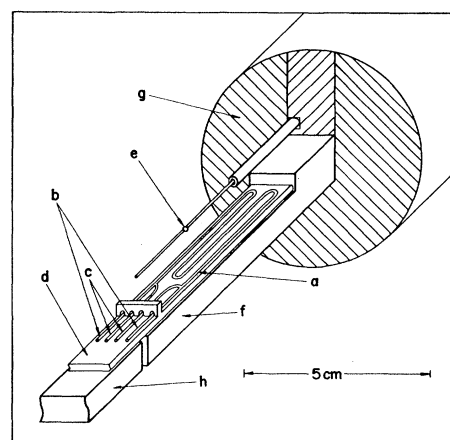


Fig. 1. Electrical resistance specimen: graphite core cut away to show the wire specimen, *a*, in relation to the furnace. *b*=current leads, *c*=potential leads, *d*=Vycor specimen support, *e*=hot junction of butt-welded Pt *versus* Pt=10% Rh thermocouple in quartz tube, *f*=end of length and x-ray lattice expansion specimen, *g*=cross section of graphite furnace core, *h*=graphite end plug.

TABLE II. Electrical resistivity of aluminum *versus* temperature. Values are corrected for thermal expansion and are based upon the standard value for Alcoa 99.995% Al at 20°C.^a Values in parentheses are interpolated.

Temp. (°C)	ρ ($\mu\text{ohm-cm}$)	Temp. (°C)	ρ ($\mu\text{ohm-cm}$)	Temp. (°C)	ρ ($\mu\text{ohm-cm}$)
14.2	2.586	310.4	6.006	570.1	9.345
16.2	2.609	(340.0)	(6.362)	(580.0)	(9.495)
19.8	2.653	415.1	7.286	581.1	9.516
(20.0)	(2.6548)	(420.0)	(7.350)	599.3	9.774
22.9	2.687	455.6	7.802	604.9	9.868
104.2	3.605	491.2	8.264	(620.0)	(10.093)
114.6	3.726	497.7	8.355	621.8	10.117
(160.0)	(4.245)	(500.0)	(8.380)	632.4	10.292
165.2	4.304	520.9	8.663	642.7	10.449
228.8	5.041	558.1	9.185	654.6	10.644
				(660.0)	(10.733)

^a See reference 17.

pared at selected temperatures to other work¹⁵⁻¹⁷ in Table I. Also shown is a comparison of derived values of the temperature coefficient of electrical resistance. The results of Pochapsky,¹⁶ obtained by a pulse technique, lie definitely above the experimental error of the present work.

Because resistivity ratios are desirable for theoretical comparisons, the measured resistance ratios were corrected for thermal expansion.¹ From direct, though necessarily crude, dimensional measurements on the specimen itself, $\rho(20^\circ\text{C}) = 2.76 \pm 0.12 \mu\text{ohm-cm}$. Therefore, the standard value of $\rho(20^\circ\text{C}) = 2.6548 \mu\text{ohm-cm}$ ¹⁷ was used to compute $\rho(T^\circ\text{C})$, which is tabulated in Table II.

IV. DISCUSSION

The measured values of electrical resistivity of aluminum at the lower temperatures require extension into the temperature interval in which appreciable concentrations of thermally generated lattice vacancy-type defects are known to be present. The results of

such an extension, described below, strongly suggest that progressively larger discrepancies at higher temperatures between the measured resistivity, $\rho(T)$, and the supposed resistivity of this aluminum without thermally generated defects, $\rho_i(T)$, do appear. Evidence that the major proportion of this discrepancy must be attributed to thermally generated defects and not merely to crystal properties such as anharmonicity¹⁸ is of two kinds. First, the discrepancy appears precisely in the temperature interval in which defect concentrations have been measured directly,¹ the magnitude and temperature dependence of the discrepancy being near that expected from measurements on quenched aluminum.¹⁹ Second, kinetic studies near room temperature on quenched material of high purity²⁰ show that the defects are indeed mobile point defects, their energy of motion being near that expected from consideration of the energy of self-diffusion (which presumably proceeds by the same defect mechanism) and their formation energy. This evidence will now be considered in detail.

A. Estimation of Lattice Resistivity, ρ_i

Aluminum is one of the most thoroughly investigated multivalent metals. It is a face-centered cubic crystal, exhibiting no phase transitions. The mean electron density between the spherically symmetric ions is very close to 3 electrons per atom, as determined by x-ray methods.²¹ The lattice vibration frequency spectrum has been studied in detail both by x-ray²² and neutron²³ diffraction techniques. Measurements of elastic constants²⁴ and thermal expansion¹ have been made over a wide temperature range. However, the

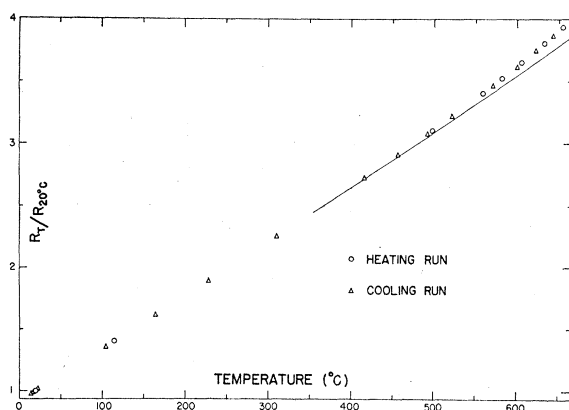


FIG. 2. Measured resistance of aluminum *versus* temperature. $R(20^\circ\text{C}) = 0.04156$ ohms. The solid curve is a visually estimated continuation of the lower temperature values.

¹⁵ L. Holborn, Ann. Physik **59**, 145 (1919); Z. Physik **8**, 58 (1921).

¹⁶ T. E. Pochapsky, Acta. Met. **1**, 747 (1953).

¹⁷ Taylor, Willey, Smith, and Edwards, Metals and Alloys **9**, 189 (1938).

¹⁸ A. A. Smirnov, Zhur. Eksptl. i Teoret. Fiz. **4**, 229 (1934).

¹⁹ W. DeSorbo and D. Turnbull, Acta Met. **7**, 83 (1959).

²⁰ W. DeSorbo and D. Turnbull, Phys. Rev. **115**, 560 (1959).

²¹ Brill, Hermann, and Peters, Naturwissenschaften **32**, 33 (1944); Bensch, Witte, and Wölfel, Z. Physik Chem. **1**, 256 (1954); **4**, 65 (1955); H. Witte and E. Wölfel, Revs. Modern Phys. **30**, 51 (1958).

²² C. B. Walker, Phys. Rev. **103**, 547 (1956).

²³ Carter, Palevsky, and Hughes, Phys. Rev. **106**, 1168 (1957); B. N. Brockhouse and A. T. Stewart, Revs. Modern Phys. **30**, 236 (1958).

²⁴ P. M. Sutton, Phys. Rev. **91**, 816 (1953).

high-temperature specific heat is not well established. A detailed analysis of the band structure of aluminum has been made by Heine.²⁵ It is concluded that the first Brillouin zone is nearly full, the third and fourth zones essentially empty, and the second zone contains almost exactly one electron per atom. A very small proportion (about 3 to 6×10^{-3} /atom) of holes is present, according to de Haas-van Alphen²⁶ and Hall-effect²⁷ studies.²⁸

No fully unobjectionable theoretical means are available for estimating the ideal lattice contribution to resistivity, unfortunately, even for the simplest metals. It is usually convenient to discuss low- and intermediate-temperature behavior and high-temperature behavior separately. High temperatures are taken to be temperatures well above the characteristic temperature, Θ . Discussions of resistivity at low- and intermediate-temperatures have been presented.²⁹ In aluminum the high-temperature interval in which experimental measurements of the lattice resistivity can be made is relatively limited, since there is less than 200° between Θ and the region in which measurable point defect contributions appear. The upper limit can be estimated as $\sim 600^\circ\text{K}$ from the increment of resistance extrapolated from quenching work¹⁹ and the known accuracy of the present measurements. Because the theoretical understanding of high-temperature resistivity is not fully established we shall resort to a variety of semiempirical methods for estimating the ideal lattice resistivity, relying to some extent upon mere consistency between different approaches in forming an estimate of the possible error involved. Three methods will be used and are described in the following.

Method I.—Since aluminum appears to have a relatively simple electron structure, we assume that its resistivity can be meaningfully compared to that of the simplest models for a metal, which all give $\rho_i \propto T\Theta^{-2}$. Because of thermal expansion and the consequent decrease in Θ , one expects that³⁰

$$d(\ln \rho_i/T)/dT \equiv d\xi/dT = -2\Theta^{-1}d\Theta/dT = 2\beta\gamma, \quad (1)$$

where $\gamma = -d \ln \Theta / d \ln V = \beta V / C_v K_T$ is a measure of the dependence of lattice mode vibrational frequencies upon volume; β is the volume thermal expansion coefficient; V is the specific volume; C_v is the specific heat at constant volume; and K_T is the isothermal

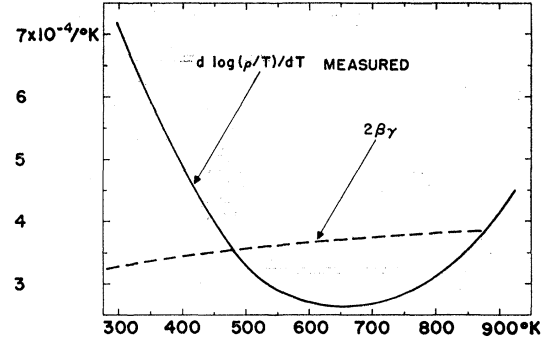


FIG. 3. Comparison of the temperature dependence of resistivity, ρ , of aluminum to the simple model $\rho \propto T\Theta^{-2}$, allowing for thermal expansion. β = volume coefficient of thermal expansion, γ = Grüneisen's parameter.

compressibility. In general, all these quantities depend upon temperature.

Figure 3 shows the variation of $d\xi/dT$ with temperature as calculated from the present measurements. The residual resistance has been subtracted from $\rho(T)$. For comparison, the Grüneisen value, $2\beta\gamma$, is plotted, deduced from Eq. (1) using published measurements,^{1,24} the high-temperature C_v being inferred from total heat measurements.³¹ The computation of $-2\Theta^{-1}d\Theta/dT$ from variation of the x-ray characteristic temperature³² yields values very close to $2\beta\gamma$ below about 600°K ; at higher temperatures there is some disagreement. On the other hand, $-2\Theta^{-1}d\Theta/dT$ from variation of the elastic characteristic temperature^{24,33} lies a factor of 1.5 to 2.3 times larger in the interval 300 to 750°K .

The value of $d\xi/dT$ given by the present measurements is of the order of magnitude expected on the simple model. In the interval immediately below 600°K , it decreases with increasing temperature, contrary to simple expectation; this behavior probably arises from other volume and temperature dependent factors such as the Fermi level and the electron-lattice interaction, and must be left for future consideration. Near 650°K an obvious new factor appears in the measured values, viz., the resistivity contribution of the thermally generated vacancies. Their appearance changes the sign of $d^2\xi/dT^2$. We expect that $\rho_i(T)$ may be estimated by allowing a continued gradual temperature variation of $d\xi/dT$ above 600°K . A possible way to allow such a smooth variation is to extend directly the integrated curve of ξ versus T . The region below 600°K is concave toward the T axis, suggesting that one choose a relation of the form

$$T = a_0 + a_1\xi + a_2\xi^2, \quad (2)$$

the constants being determined from $\rho(T)$ values in the interval 430 – 610°K . We note that the narrowness of

²⁵ V. Heine, Proc. Roy. Soc. (London) **A240**, 340, 354, 361 (1957).

²⁶ E. M. Gunnerson, Phil. Trans. Roy. Soc. (London) **A249**, 299 (1957).

²⁷ W. Kapp and F. Stangler, Z. Physik **154**, 486 (1959).

²⁸ Note added in proof.—A reconsideration of Gunnerson's data has recently been presented by W. A. Harrison, Phys. Rev. **116**, 555 (1959).

²⁹ See, for example, D. K. C. MacDonald, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, p. 137.

³⁰ N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, New York, 1936).

³¹ J. H. Awwery and E. Griffiths, Proc. Phys. Soc. (London) **38**, 378 (1926).

³² E. A. Owen and R. W. Williams, Proc. Roy. Soc. (London) **A188**, 509 (1947).

³³ S. L. Quimby and P. M. Sutton, Phys. Rev. **91**, 1122 (1953).

TABLE III. Comparison of the different extrapolation methods discussed in Sec. IV A of the text. Method I uses $T=a_0+a_1 \ln(\rho/T)+a_2 \ln^2(\rho/T)$; Method II uses $\rho=b_0+b_1T+b_2T^2$; Method III uses $R(T)/R(20^\circ\text{C})$ extended by eye.

Temp. ($^\circ\text{C}$)	ρ_i ($\mu\text{ohm-cm}$) Method			ρ ($\mu\text{ohm-cm}$) Measured	$[\rho - \rho_i]^a$ ($\mu\text{ohm-cm}$)
	I	II	III		
693	7.33 ₇	7.33 ₇	7.33 ₆	7.350	0.01 ₃
773	8.33 ₄	8.33 ₃	8.33 ₂	8.380	0.04 ₇
853	9.35 ₁	9.35 ₁	9.34 ₇	9.495	0.14 ₄
893	9.86 ₇	9.86 ₃	9.86 ₅	10.093	0.22 ₅
933	10.38 ₈	10.39 ₀	10.38 ₂	10.733	0.34 ₃

^a ρ_i from Method II.

the temperature interval where the high-temperature lattice resistivity is observable for aluminum is emphasized by this method.

Method II.—As another technique, we take the commonly used high-temperature representation of the direct data

$$\rho_i = b_0 + b_1T + b_2T^2, \quad (3)$$

with the constants determined by $\rho(T)$ values in the region 430–610°K. This has no direct justification, except possibly as an expansion at not too high temperature of the integral of Eq. (1) or of some other theoretical analysis based upon anharmonic lattice behavior. In any case, there is at present no straightforward identification of the coefficients b_i with other physical properties. Equation (3) is a well-behaved analytical expression that fits the data within experimental error in the temperature interval and, in addition, varies smoothly at high temperature. The values of the coefficients used here are $b_0 = -0.4095 \mu\text{ohm-cm}$, $b_1 = 1.0028 \times 10^{-2} \mu\text{ohm-cm/deg K}$, and $b_2 = 1.656 \times 10^{-6} \mu\text{ohm-cm/deg K}^2$.

Method III.—Most directly, one may use Fig. 2, which shows ratios $R(T^\circ\text{C})/R(20^\circ\text{C})$, and continue the apparent curve by eye above $\sim 600^\circ\text{K}$. The relative size of the defect contribution to resistance must be quite appreciable if this scheme is to have any validity. Values of $\rho_i(T)$ are then obtained after correction of $R(T^\circ\text{C})/R(20^\circ\text{C})$ for thermal expansion and use of $\rho(20^\circ\text{C})$.

The results of the different methods employed here are collected in Table III. They all fall in the same range. We arbitrarily adopt the convenient Method II for purposes of later calculation.

Other more elaborate methods of extrapolation can be envisaged. For example, one might use the Bloch-Grüneisen relation

$$\rho/T = \text{const}(T/\Theta)^4 J_5(\Theta/T) \quad (4)$$

in order to use experimental fitting points at temperatures lower than those employed in Methods I and II above. For satisfactory agreement with data, however, this requires an additional factor of the form $(1+c_1T+c_2T^2)$. Even aside from this additional empirical factor, however, the theoretical relationship itself has been criticized.²⁹

Finally, we obtain a crude estimate of possible extrapolation error by considering Fig. 3. A simple assumption which should serve to estimate limiting values of $\rho_i(T)$ is given by letting $d\xi/dT \rightarrow \text{constant} = 2.50 \times 10^{-4}$ per degree at high temperature. This gives $\rho_i(993^\circ\text{K}) = 10.47 \mu\text{ohm-cm}$, to be compared with the values given in Table III.

B. Defect Contribution to the Resistivity and the Resistivity of Monovacancies

The total resistivity attributed to all of the point defects at high temperature may be determined by taking the difference between the measured resistivities as estimated in the previous section. These values are given in Table III.

Each family of defects will make its own contribution to the total resistance increment, $\Delta\rho$, and it remains to consider the individual contributions. As shown in the preceding paper¹ the only vacancy-type defects present in appreciable concentrations are probably monovacancies and divacancies, and therefore

$$\Delta\rho = A_{v1}c_{v1} + A_{v2}c_{v2}, \quad (5)$$

where c_{v1} and c_{v2} are the monovacancy and divacancy concentrations and where the coefficients may depend upon both the concentration and the temperature.

A relatively accurate value of A_{v1} may be obtained by noting that c_{v2} is appreciably smaller than c_{v1} (see Table III of reference 1) and that probably $A_{v2} = 2A_{v1}$ within 10% or so.³⁴ With these results

$$\Delta\rho \simeq A_{v1}(c_{v1} + 2c_{v2}) \simeq A_{v1}(\Delta N/N) \quad (6)$$

where $\Delta N/N$ is the total concentration of thermally generated sites.

In view of the divacancy estimate $A_{v2} = 2A_{v1}$, the concentration dependence of A_{v1} should be very small, since c_{v1} never exceeds about 10^{-3} .

We are primarily interested in A_{v1} at low temperature, because the residual resistivity per monovacancy is the quantity measured in recent quenching work^{19,20} and is the value most easily estimated theoretically.

³⁴ For copper it has been estimated [A. Seeger and H. Bross, J. Phys. Chem. Solids, **6**, 324 (1958)] that the resistivity of a divacancy is only about 10% less than that of two isolated vacancies.

Measurements on aluminum containing dilute solutions of magnesium, zinc, germanium, or silver³⁵ give the temperature dependence of A_{v1} directly, i.e., the deviations from Matthiessen's rule, because lattice vacancies and chemical impurity atoms are both localized defects. Independent of solute it is found that at temperatures above 77°K the impurity resistivity is increased by a constant factor 1.12 over the residual value. Therefore the $\Delta\rho$ to be used in Eq. (6) is $(\rho - \rho_i)/1.12$.

Additional temperature dependence of A_{v1} may arise from changes in the form and dimensions of the defects with temperature. We note that the experimental results shown in Fig. 4 of the preceding paper and in Fig. 4 of the present paper indicate that $\Delta\rho$ and $\Delta N/N$ appear to have essentially the same temperature dependence. This result is consistent with a relatively small temperature dependence of A_{v1} as seen from Eq. (6).

At the melting point we have $\Delta\rho = (1.12)^{-1}(\rho - \rho_i) = 0.30 \mu\text{ohm-cm}$ and $\Delta N/N = (9.4 \pm 0.4) \times 10^{-4}$ from the direct length and lattice expansion measurements.¹ This gives $A_{v1} = 3 \mu\text{ohm-cm/atom } \%$ monovacancies.

Because no theoretical estimates of A_{v1} for monovacancies in aluminum have yet been made with which to compare the experimental value of $3 \mu\text{ohm-cm/atom } \%$, we cite here some circumstantial evidence which indicates that this value may be correct. Consider first copper, a thoroughly investigated example.³⁶ The results of Linde,³⁷ as explained by Mott³⁰ on the resistivity of dilute solutions of atoms of different valency in copper, give that the incremental resistivity, $\Delta\rho$, is given by

$$\Delta\rho = a + bZ^2, \quad (7)$$

where Z is the valence difference between solute and solvent atoms, and a and b are constants in each row of the periodic table, provided that inner shell complications do not intervene as for transition metal solutes. For nickel in copper, $\Delta\rho(\text{Ni}) = 1.2 \mu\text{ohm-cm/atom } \%$.^{37,38} Further, for a vacancy in copper, for which Z is presumed to be of the same sign and magnitude, $\Delta\rho(\text{vac.}) \approx 1.2 \mu\text{ohm-cm/atom } \%$.³⁶ Now for magnesium in aluminum, $\Delta\rho(\text{Mg}) = 0.4 \mu\text{ohm-cm/atom } \%$ ^{35,38} from which Eq. (7) gives $b = 0.4 \mu\text{ohm-cm}$ on the assumption that $a = 0$ because magnesium and aluminum are in the same period. A vacancy in aluminum may have Z near 3 from which Eq. (7) then gives $\Delta\rho(\text{vac.}) \approx 3.6 \mu\text{ohm-cm/atom } \%$, near the experimental value of 3. Here inner shell complications may not enter. This question requires further detailed

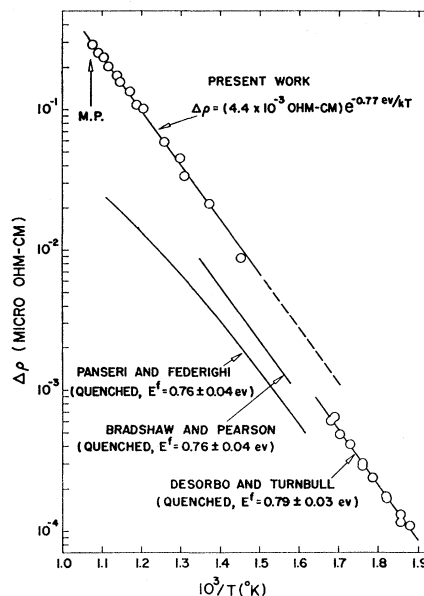


FIG. 4. Comparison of the residual resistance values, $\Delta\rho$, attributed to thermally generated vacancy-type defects in aluminum, from different investigations.

consideration, of course, but tentative agreement for this very crude model is obtained.

C. Comparison with Other Measurements

Values of $\Delta\rho$ obtained from the present high-temperature measurements are shown in Fig. 4. Method II was used in extending $\rho_i(T)$, and the supposed difference has been reduced by a factor $(1.12)^{-1}$ for Matthiessen rule deviations.³⁵ The data are well fitted by the relation

$$\Delta\rho = (4.4 \times 10^{-3} \text{ ohm-cm}) \exp(-0.77 \text{ eV}/kT).$$

The value of formation energy, $E^f = 0.77 \text{ eV}$, derived from the present data is in good agreement with the corresponding value of $E^f = 0.76 \text{ eV}$ derived in the preceding paper¹ from the measurements of the total concentration of vacancy-type defects. This result appears quite consistent with our discussion and use of Eq. (6). This value added to the monovacancy motion energy of 0.65 eV measured in high purity quenched material²⁰ yields a value 1.42 eV for the energy of self-diffusion by this defect mechanism. This is in satisfactory agreement with the value $1.4 \pm 0.1 \text{ eV}$ given by nuclear magnetic resonance techniques³⁹ and with the value $1.43 \pm 0.08 \text{ eV}$ obtained from a semi-empirical analysis of alloy diffusion data.⁴⁰

We note that the entropy of formation cannot be obtained from the present data but can be derived unambiguously only from direct measurements of defect concentration.¹

³⁵ P. Alley and B. Serin, Phys. Rev. **116**, 334 (1959).

³⁶ For a review see F. J. Blatt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4, p. 200.

³⁷ J. O. Linde, Ann. Physik **15**, 219 (1932).

³⁸ A. P. Gulyaev and E. F. Trusova, Zhur. Tekh. Fiz. S.S.S.R. **20**, 66 (1950).

³⁹ J. J. Spokas and C. P. Slichter, Phys. Rev. **113**, 1462 (1959).

⁴⁰ A. S. Nowick, J. Appl. Phys. **22**, 1182 (1951).

There is considerable interest in comparing the present derived values of $\Delta\rho$ with values of $\Delta\rho$ obtained in quenching work under different conditions and for prequenching temperatures as low as 530°K. Also shown in Fig. 4 are values of the residual resistance added by quenching, according to various investigators.^{19,41,42} It is evident that while at the lowest temperatures all the quenching investigations appear to give nearly the same value of E' , within the respective stated probable errors, the values of $\Delta\rho$ at a given temperature vary over a broad range. Further, the present $\rho_i(T)$ values estimated at high temperatures from the various extrapolation methods lead to an even larger $\Delta\rho$. Some difficulty is therefore encountered in comparing the $\Delta\rho$ and E' values derived from the present data with the values from the quenching work.

Possible contributions to these discrepancies are of three types. They are (1) failure of quenching methods to retain the entire equilibrium concentrations of defects, (2) the presence of an appreciable divacancy contribution to the present $\rho(T)$ values at the highest temperatures, and (3) systematic error in the estimation of $\rho_i(T)$.† We consider these in turn.

It is evident that the equilibrium defect concentrations may not be retained because faster quenching rates usually produce a larger $\Delta\rho$ from a given prequenching temperature. Bradshaw and Pearson⁴¹ obtain an increase in $\Delta\rho$ of about 65%, with quenching rates near 3×10^4 deg/sec, over that reported by Panseri and Federighi⁴² at lower rates. Coupled with the larger $\Delta\rho$ is a higher temperature, T_m , above which apparent loss of defects during quenching begins to occur as indicated by curvature in the $\log\Delta\rho$ versus T^{-1} relation. An analysis of this phenomenon in terms of the energy of motion of the defects has been published.⁴³ On the other hand, while the $T_m \approx 320^\circ\text{C}$ of DeSorbo and Turnbull¹⁹ is lower than the $T_m \approx 470^\circ\text{C}$ of Bradshaw and Pearson,⁴¹ as expected from their lower initial quenching rate of about 8×10^3 deg/sec,⁴⁴ their $\Delta\rho$ is higher by 40%. Variations in sample purity would not appear to be responsible because DeSorbo and Turnbull obtain similar $\Delta\rho$ values for material having residual

resistivity ratios of 800¹⁹ and 4200.²⁰ A similar result is obtained for high chemical impurity concentrations in platinum.⁴⁵ The cause of the apparent agreement in E' values for different quenching rates remains obscure. A definite conclusion is that a given quenching technique cannot be assumed to retain the equilibrium concentration of defects simply because it gives a satisfactory E' value.

Our preceding work¹ indicates that at the prequenching temperatures of the recent quenching work¹⁹ only monovacancies were present, whereas there may be a significant divacancy contribution to the present high temperature equilibrium measurements. From calculations as in reference 1 we conclude that the value E' for monovacancies derived from the present resistivity data may actually be reduced to about 0.75 ev if the divacancy binding energy, G_{v2} , is as large as 0.25 ev. This E_{v1}' value is seen to agree within expected experimental error with other values. Further, the divacancy contribution at the melting point to resistivity for $G_{v2} = 0.25$ ev would be

$$[2c_{v2}/(c_{v1} + 2c_{v2})](\rho - \rho_i)/(1.12) \approx 0.05$$

$\mu\text{ohm-cm}$ or about $\frac{1}{3}$ of the discrepancy.

Lattice anharmonicity, or other electron-lattice type contribution which is volume or temperature dependent, might enter in a progressive way at temperatures above about 600°K and thus defy direct experimental detection. The values of $\rho_i(T)$ as estimated in Sec. IV A might therefore be too small and the derived $\Delta\rho$ be too large. An upper limit to such effects can be firmly established. They are less than about $\frac{1}{6} \mu\text{ohm-cm}$ at the melting point from the extreme assumptions that the divacancy concentration is negligible at high temperature and that DeSorbo and Turnbull retain all the vacancies present at the prequenching temperature. The crudely estimated limit on extrapolation error obtained at the end of Sec. IV A corresponds to about $\frac{1}{2}$ of the discrepancy.

In aluminum the disagreement between equilibrium measurements and the more recent quenching work is not large, and can probably be ascribed to a combination of the above factors.

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We wish to acknowledge a useful discussion on quenching with Professor J. S. Koehler.

⁴⁵ F. J. Bradshaw and S. Pearson, *Phil. Mag.* 2, 1387 (1956).

⁴¹ F. J. Bradshaw and S. Pearson, *Phil. Mag.* 2, 570 (1957).

⁴² C. Panseri and T. Federighi, *Phil. Mag.* 3, 1223 (1958).

† An additional contribution which is probably smaller, but still worth mentioning, is a decrease in quenched resistivity due to non-equilibrium vacancy aggregation occurring during or directly after quenching.

⁴³ F. J. Bradshaw and S. Pearson, *Phil. Mag.* 1, 812 (1956).

⁴⁴ D. Turnbull (private communication).