

Resistivity of Lattice Vacancies in Gold*

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Resistivity measurements on pure gold were performed at high temperatures in equilibrium conditions. The resistivity increment compared to the extrapolated low temperature course is connected with an activation energy lying in the range from 0.70 to 0.80 eV. The results are compared with former experimental results and the possibility is discussed to distinguish between the effect of vacancies and that of lattice vibrations.

§ 1. Introduction

For some time there exist a discrepancy between the values of activation energy of lattice vacancy formation in gold derived either from rapid quenching experiments or equilibrium high temperature data. Resistivity measurements after rapid quenching led to values $E_F=0.98$ eV¹⁾, and 0.95 eV²⁾. Calorimetric study of quenched-in vacancies in gold foils by De Sorbo³⁾ gave 0.97 eV.

Contrary to the quenching experiments the activation energy derived from high temperature measurements by Meechan and Eggleston⁴⁾ was only 0.67 eV**, whereas Gercricken⁵⁾ found 0.71 eV. Combined dilatometric and lattice parameter measurements were proposed by Gercricken⁶⁾ and led to the formation energy 0.74 eV. Recently Takamura⁷⁾ found from dilatometric measurements extrapolated to zero diameter the value 0.98 eV. Precise measurements of $\Delta l/l$ and $\Delta a/a$ carried out on the same pure gold specimen by Simmons and Balluffi⁸⁾ led to the activation energy 0.94 eV.

It is obvious that different methods give comparable results in gold with exception of the equilibrium resistivity measurements. In these measurements the whole resistivity increment has been usually identified with

the resistivity of equilibrium vacancies. This was seriously criticized by Nicholas⁹⁾. Now two questions arise: a) whether the low activation energies found in Refs. (4) and (5) are correct and b) what is the contribution of lattice vacancies to this increment. These are important questions, for a good agreement between both kinds of measurements was achieved in aluminium¹⁰⁾.

In the following we shall describe our experimental procedure of resistivity measurements at high temperatures, experimental results and their discussion.

§ 2. Experimental Part

Gold wires of 0.1 mm diameter supplied by Johnson & Matthey, London (purity 99.999%), were used as specimens. The wire (about 25 cm long) was wound bifillary on a four-hole capillary tube made of Degussit (Degussa, Hanau) and then placed in a tube made of sintered corundum (made in GDR) in an electrically heated furnace (see Fig. 1). The potential and current leads were made of the same material as the specimen. Oxygen free nitrogen or argon steadily flowed through the tube containing the specimen.

Measurements in the low temperature range up to 250°C were carried out in a stirred silicon oil bath (silicon oil OE 4018/50 centipoise, VEB Chemiewerk Nünchritz, GDR), because the precision of the lower temperature measurements in the furnace is usually not high enough.

Before the measurement the specimen was annealed for some hours in nitrogen at 1000°C. The resistance of the sample was checked at 0°C both before and after the measurements. Similarly as in our previous measurements (not yet published) a steady slight resistivity

* Presented by the chairman of the session. A few papers in the final program which could not be presented by the author are included exceptionally in this Proceedings.

** Dr. Meechan reported to us that Dr. G.H. Kinchin at Harwell, England, has pointed out some ambiguity existing in the analysis of the gold data. If the experimental point at 17°C is ignored, a superior fit is obtained with the quadratic expression at low temperatures and E_F is slightly less than 1.1 eV.

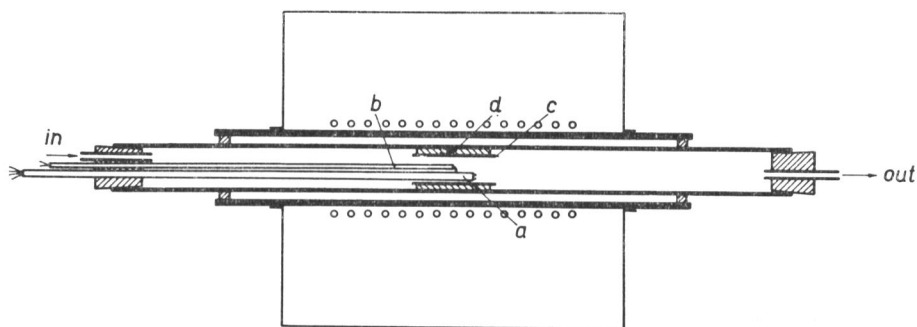


Fig. 1. Experimental assembly: (a) specimen, (b) thermocouple, (c) protecting corundum tube, (d) copper or gold tube.

increase during the stay at high temperatures, caused partly by the change of geometrical dimensions (*e.g.* due to evaporation) and partly by growing of the impurity content was observed, so that the stay at high temperatures should have been as short as possible.

The resistance of the specimen was measured by comparing it with the normal resistors Metra (1 ohm) by means of a 5-dial Diesselhorst-type precision potentiometer (VEB, GDR). The temperature of the sample was determined by means of a Pt/Pt, Rh 10 % thermocouple, supplied by Heraeus (GFR) which was calibrated at several normal thermometric points, including the gold point. A Diesselhorst-type 5-dial potentiometer R-306 of Soviet origin was used for measuring the thermoelectric force. The thermocouple was placed near to the surface of the supporting capillary tube.

§ 3. Results of Measurements

Several experiments in air, nitrogen and argon were carried out, with slightly different results, corresponding to changing experimental conditions. The reason for these differences was the different contamination of the specimens at high temperatures. For this paper we have chosen one of two measurements carried out with the same sample, the two being almost identical. The results of resistance measurement with this sample are summarized in Table I together with corrected and deduced values. For dilatation correction of ρ_T the values of α_T derived from Ref. (8) were used. Before the measurement the resistance of the sample at 0°C was $R_0 = 0.42566 \Omega$, after the measurement $R_0 = 0.42641 \Omega$. In high temperature measure-

ments this increase is not an essential one and may be neglected.

Table I. Experimental results of the resistance measurement at high temperatures

$T [^\circ\text{C}]$	$R_T [\Omega]$	$\rho_T [\mu\Omega\text{cm}]$	$\log(\rho_T/T) + 9$
0.0	0.42566	2.2500	0.9160
22.3	0.46206	2.4424	0.9175
54.1	0.51501	2.7237	0.9205
81.2	0.56117	2.9690	0.9234
104.7	0.60146	3.1831	0.9257
128.2	0.64221	3.4001	0.9281
156.9	0.69236	3.6671	0.9309
180.8	0.73440	3.8909	0.9332
205.3	0.77833	4.1253	0.9357
229.4	0.82149	4.3558	0.9380
255.0	0.86765	4.6029	0.9404
278.4	0.91153	4.8365	0.9430
327.5	1.00220	5.3219	0.9475
388.9	1.11888	5.9474	0.9535
435.1	1.21012	6.4369	0.9586
474.4	1.28861	6.8592	0.9627
537.8	1.41862	7.5587	0.9695
591.1	1.53166	8.1691	0.9756
643.6	1.64684	8.7912	0.9819
705.1	1.78654	9.5474	0.9895
750.9	1.89483	10.1351	0.9956
820.3	2.06499	11.0594	1.0050
867.6	2.18686	11.7236	1.0119
927.4	2.34725	12.5971	1.0210

In this table the value of $\rho_0 = 2.25 \mu\Omega\text{cm}$ has been adopted for the temperature 0°C.

§ 4. Discussion of Results

When we suppose that the Matthiessen's rule and the Mott-Jones theory hold the resistivity of a metal at temperature T may

be expressed as a sum of three terms, namely

$$R_T = R_i + AT \exp(2\bar{\alpha}\gamma T) + B \exp(-E_F/kT), \quad (1)$$

where R_i is the residual resistance due to impurities and other imperfections, the concentration of which is not temperature dependent. The second term represents the lattice resistivity according to Mott and Jones¹¹⁾ and the last term is due to equilibrium vacancies. In pure metals $R_i \ll R_T$ at room temperature and above it and therefore it can be neglected or when necessary measured at helium temperature.

When plotting the dependence of $\log(R_T/T)$ from the temperature we should get a straight line at lower temperature where the last term is negligible. At higher temperatures a contribution of equilibrium vacancies should appear. The preceding authors had simplified this method using only the two first terms of the extension of $\exp(2\bar{\alpha}\gamma T)$ and fitting the quadratic curve at lower temperatures and then extrapolating it to the higher temperatures. The difference between the experimental and the extrapolated values was then attributed to the effect of vacancies.

We have also tried to use the quadratic approximation for the extrapolation method, but this proved in many cases to be not very reliable. The method of quadratic extrapolation

was seriously criticized by Nicholas,⁹⁾ who recommends to check the validity of the relation

$$\frac{d}{dT}[\ln(R_T/T)] = 2\bar{\alpha}\gamma, \quad \bar{\alpha} = 3\alpha,$$

by plotting $\ln(R_T/T)$ as a function of T . We have changed this a little using ρ_T instead of R_T . In this way a straight line may be drawn in the temperature range from 0 to 500°C. (Fig. 2). At higher temperatures a distinct deviation occurs which is obviously due partly to lattice vacancies and partly to the anharmonicity of lattice vibrations.

The slope of the straight part of the curve gave

$$2\bar{\alpha}\gamma = 2.32 \times 10^{-4}.$$

When the logarithm of the extra-resistivity $\Delta\rho_T$ determined as the difference between the experimental and extrapolated curve is plotted as a function of reciprocal temperature, the straight line (a) in Fig. 3 is obtained, giving an activation energy 0.70 eV. This is apparently of the same order as in papers (4) and (5). For comparison, the result of quenching experiments by Bauerle and Koehler¹⁾ are plotted in the same figure (curve (c)). In our measurements the resistivity increment corresponding to the vacancy concentration at 1000°C is about seven times larger than

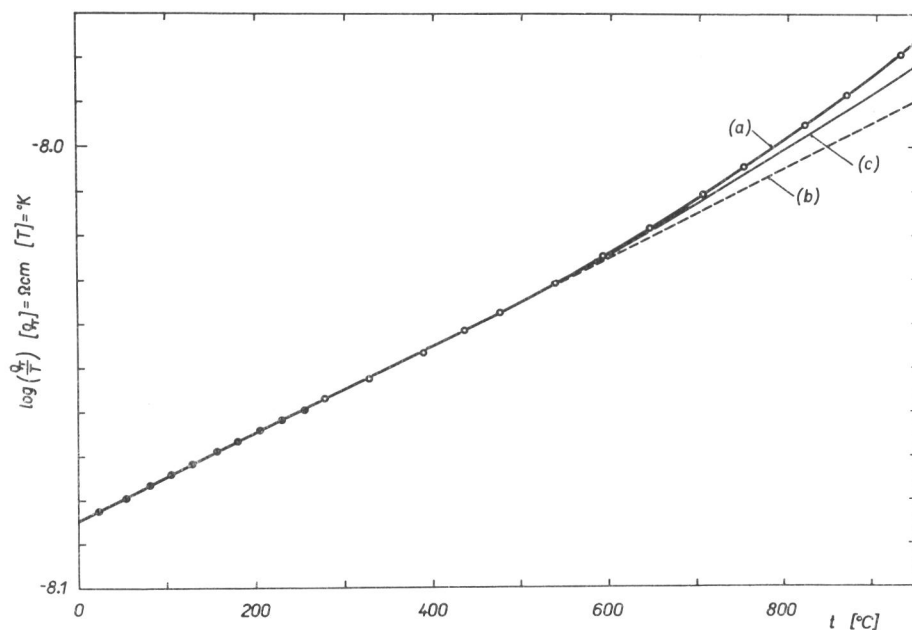


Fig. 2. Temperature dependence of $\ln(\rho_T/T)$ of gold: (a) experimental curve, (b) extrapolated straight line, (c) extrapolated curve.

in quenching experiments, and the activation energy is substantially lower.

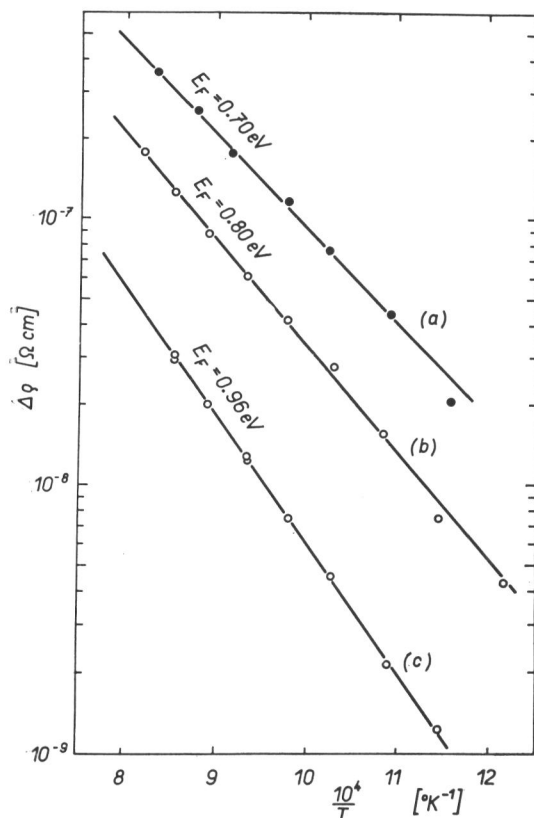


Fig. 3. Vacancy formation energy of gold: (a) extrapolation by straight line, $E_F = 0.70$ eV, (b) extrapolation by a curve, $E_F = 0.80$ eV, (c) quenching experiments of Bauerle and Koehler¹¹, $E_F = 0.94$ eV.

Since we know the temperature dependence of α_T , we could calculate γ_T for the straight part of the curve (a) in Fig. 2, but this cannot be used at higher temperatures.*

We must therefore look for another method of extrapolating the second term in Eq. (1) to higher temperatures bearing in mind that the increased anharmonicity should be respected. In consequence to the anharmonicity the Debye temperature falls. This may be deduced from the relation

* $2\alpha\gamma$ is constant up to 500°C, α_T steadily rises and therefore γ decreases with the temperature, though Grüneisen theory supposed γ to be constant. Similar disagreement was found in checking the validity of the relation $(R_T/T) \propto \alpha_T$. In the temperature range from 500 to 1000°C the value of $(\alpha_T \cdot T/R_T)$ is constant within about 10 % only.

$$\frac{d}{dT}(\ln \Theta) = -\frac{1}{V} \frac{dV}{dT} \frac{d \ln \Theta}{d \ln V} = -\bar{\alpha}\gamma. \quad (2)$$

Knowing the temperature dependence of the Debye temperature, we could determine $2\bar{\alpha}\gamma$ and thus the slope of $\log(\rho_T/T)$ in Fig. 2 beyond the linear region, but we have found no measurements of $\Theta = \Theta(T)$ for gold. Moreover it is not certain whether the precision of these measurements performed usually by X-ray technique would be sufficient for our purposes.

We have avoided the lack of experimental data in the following way. We can suppose the Grüneisen theory as a first approximation and thus

$$\Theta_T/\Theta_r = (V_r/V_T)^\gamma = (a_r/a_T)^{3\gamma} \quad (3)$$

holds. Θ_T , V_T and a_T are Debye temperature, volume and lattice parameter at temperature T , respectively. Index r denotes the values at some reference Debye temperature Θ_{Tr} . In this approximation the Grüneisen constant is supposed to be constant and equal to 3. (The highest value of γ in our measurements is 2.8). Using the lattice parameter expansion data of Simmons and Balluffi⁸) we have plotted the temperature dependence of $\log \Theta_T$ in Fig.

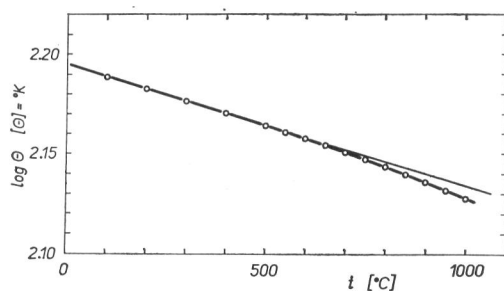


Fig. 4. Temperature dependence of $\log \Theta_T$, derived for $\gamma = 3$.

4. As reference Debye temperature $\Theta_{Tr} = 156^\circ\text{K}$ taken from (12) was chosen. The points lie on a straight line till 500°C, the slope of which gives $2\bar{\alpha}\gamma = 2.7 \times 10^{-4}$. This value is in agreement with the value 2.3×10^{-4} , derived from resistivity measurements. $2\bar{\alpha}\gamma$ is increasing at temperatures above 500°C. We have thus obtained the temperature dependence of $(2\bar{\alpha}\gamma)'$ by supposing originally that γ is constant. Now we suppose that the slope of the true lattice resistivity curve should change in the same proportions as $(2\bar{\alpha}\gamma)'$ in Fig. 4 does. Then starting at the end of the

straight interval of the curve (a) in Fig. 2 we may plot the curve (c), representing the lattice resistivity. The resistivity increment measured from this curve leads to the activation energy $E_F=0.80$ eV, which is closer to the well established formation energy values derived from quenching experiments.

In contrast to this, another very simple approach may be used to find the lattice resistivity itself. We cannot prove that Matthiessen's rule holds for vacancies at high temperatures, but we can suppose it neglecting any temperature dependent interaction between defected and lattice resistivities. Then by subtracting the computed resistivity of equilibrium vacancies ($1.5 \mu\Omega$ cm per at. % vac.) from the experimental curve, the true lattice resistivity would be obtained.

§ 5. Conclusions

In reviewing our work on high temperature resistivity of gold, we would like to emphasize the following points:

The equilibrium methods determine the increment as a difference of two large values and one of the values, the extrapolated one, is based on an approximative theory and therefore is not fully reliable. Also the quenching data cannot be used without precaution to separation of the effect of vacancies, as they partly depend on quenching rate (in experiments of Bauerle and Koehler¹¹ the doubling of quenching rate led to 20% increase of extra-resistivity). Besides this the scattering power of vacancies at high temperatures may be different from that at low temperatures.

The values of resistivity increment strongly depend on the precision of extrapolation method and the lower temperatures resistivity values are decisive. Therefore a higher precision is needed and this may be accomplished by measuring in a liquid bath. The extrapolation method proposed by Nicholas seems to give superior results in comparison

with the quadratic approximation. Our method of extrapolation does not solve the problem, though its results are better than those of both preceding methods—the resistivity increment at 1000°C ($c_v=5\times 10^{-2}\%$) is about $5 \mu\Omega$ cm/at. % of vacancies. Also the activation energy $E_F=0.80$ eV is nearer to the true value, slightly lower than 1 eV. In fact, without an improved theory any extrapolation will be speculative. Only improved theory and higher accuracy in resistivity measurements may help to solve this problem.

Acknowledgement

We should like to extend our hearty thanks to Dr. Nicholas, Dr. Simmons and Dr. Meehan for their critical comments and helpful advices and to the members of Metal Physics Department of the Institute of Solid State Physics at Prague for steady support and help. Especially the assistance of Mr. Andrie and Mr. V. Ballik in measurements was very appreciated.

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DISCUSSION

Simmons, R. O.: I would like to emphasize what the authors point out concerning the magnitude of the resistivity increment attributed to the thermally generated defects. This magnitude is unexpectedly large, and would require an effect on the electron scattering which is 5 to 10 times as large as the resistivity increments obtained in quenching experiments.

Klemens, P. G.: When analysing high temperature electrical resistance data one must consider the possibility of two-phonon processes contributing to the resistivity or T^2 term. Old data shows such an up turn to occur both in Au and Cu at about the same temperature, which is consistent with the theory of such two-phonon processes.

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Equilibrium Concentration of Lattice Vacancies in Lead and Lead Alloys

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The equilibrium concentration of vacancies near the melting point of pure lead and of a number of dilute lead solid solutions has been measured. The method involves comparison of microscopic thermal expansion with the microscopic expansion obtained from precision X-ray lattice parameter measurements. The results on dilute binary solid solutions of lead with In, Tl, Sn and Bi show no detectable vacancy concentration, corresponding to a mole fraction $\leq 5 \times 10^{-5}$. On the other hand, the data for pure lead indicate a vacancy concentration of 20×10^{-5} at the melting point. The explanation for these surprising results is not apparent.

§ 1. Introduction

In recent work on point defects in metals there has been considerable interest in the interaction between impurities and vacancies. Such interaction has usually been studied by observing the effect of impurities on the annealing kinetics of vacancies in quenched samples.^{1)–3)} Another manifestation of such interactions would be the effect of impurities on the equilibrium concentration of vacancies at elevated temperatures, *i.e.* near the melting point of the metal. This effect is easily computed with the aid of simplifying assumptions. Customarily, it is assumed⁴⁾ that the energy of formation of a vacancy in a nearest neighbor position to an impurity is lowered by ε_b , and that there is no effect at greater distances. Thus ε_b is the vacancy-impurity binding energy. On the basis of this assumption, and for ε_b not too large, one readily obtains for the ratio of the mole fraction of vacancies (c_v^s) in dilute f.c.c. solid solution, to that in the pure metal (c_v^0), the approximate expression

$$c_v^s/c_v^0 = 1 - 12c_i + 12c_i \exp(\varepsilon_b/kT) \quad (1)$$

where c_i is the concentration of solute. This ratio is unity for $c_i=0$, or $\varepsilon_b=0$. For example, in 1% alloys ($c_i=0.01$), which may still be regarded as dilute enough to show simple impurity-vacancy interactions, the ratio c_v^s/c_v^0 at the melting point of Pb increases from 1.7 for $\varepsilon_b=0.1$ ev, to 6.5 for $\varepsilon_b=0.2$ ev. The total vacancy concentration can therefore be greatly affected by alloying if there is a favorable (*i.e.* positive) binding energy ε_b . On the other hand, for negative ε_b (signifying vacancy-solute repulsion), the effect of small amounts of impurities on the vacancy concentration according to the above simple theory will not be very great. Thus, even for $\varepsilon_b=-\infty$, Eq. (1) gives only a 12% reduction in vacancy concentration for 1% solute.

The most direct method for measurement of the equilibrium concentration of vacancies near the melting point is by comparison of thermal expansion as measured macroscopically in a dilatometer, with that obtained (by X-rays) from the change in lattice parameter with temperature. The method is by now well known, and has been applied to a number of pure metals.^{5), 6)} If L_0 and a_0 are values of