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RESISTIVITY OF LATTICE VACANCIES IN GOLD

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Abstract:

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 0.92 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.

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 ev 1), and 0.95 ev 2). Calorimetric study of quenched-in vacancies in gold foils by De Sorbo 3) gave 0.97 ev.

In contrary to the quenching experiments the activation energy derived from high temperature measurements of Meechan and Eggleston 4) was only 0.67 ev *), whereas Gererikes 5)

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Footnote: *) 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. We shall have opportunity to remind this fact later (see page xxx).

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found 0.71 ev. Combined dilatometric and lattice parameter measurements were proposed by Gerciriken 6) and led to the formation energy 0.74 ev. Recently Takamura 7) found from dilatometric measurements extrapolated to zero diameter the value 0.98 ev. Precise measurements of ρ and a/a carried out on the same pure gold specimen by Simmons and Balluffi 8) 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 Nicholas 9). Now two questions arise: a) whether the low activation energies found in 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 achived in aluminium 10).

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

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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 bifilary on a four-hole capillary tube made of Degusit (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

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Caption to Figure 1.:

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

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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 CE 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 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 convent was observed, so that the stay at high temperatures should have been as short as possible.

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The resistance of the specimen was measured by comparing it with the normal resistors Metra (1 ohm) by means of a 5-dial Diessel-horst-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 next to the surface of the supporting capillary tube.

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 summarised in Table I together with corrected and deduced values. For dilatation correction the values of derived from 8) were used. Before the measurement the resistance of the sample at 0 °C was R_0 = 0,42566 , after the measurement R_0 = 0,42641 . In high temperature measurements this increase is not an essential one and may be neglected.

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Table I.

Experimental results of the resistance measurement at high temperatures

t °C	R_t	ρ_t μ Ω cm	log ρ_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
82.2	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	0.9308
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	1.28851	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
785.1	1.78654	9.5474	0.9895
750.9	1.88483	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 ρ = 2.25 μ Ω cm has been adopted for the temperature 0 °C .

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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

$$R_T = R_1 + A\,T \exp(2\quad T) + B \exp(-E_v/kT), \qquad (1)$$

where R_1 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 Jones 11) and the last term is due to equilibrium vacancies. In pure metals R_1 R_2 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 temperatures 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 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 criticised by Kinchine 9), who recommends to check the validity of the relation

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$$\frac{d}{dT} \ln (\rho_T T) = \alpha \quad , \quad = \beta \quad ,$$

by plotting ln $\rho_T T$ as a function of T. We have changed this a little using $_T$ instead of R_T. In this way a straight line may be drawn in the temperature range from 0 to 500 °C. (Fig. 2)

Caption to Fig.2.:

Fig. . Temperature dependence of ln ($_T$ T) of gold: (a) experimental curve, (b) extrapolated straight line, (c) extrapolated curve (see page xxx).

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

$$\alpha = 2,34 \times 10^{-4} .$$

When the logarithm of the extra-resistivity $_T$ 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.

Caption to Fig. 3.:

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 Koehler 1), E_F = 0,94 ev.

This is apparently of the same order as in papers 4) and 5). For comparison, the result of quenching experiments by Bauerle and

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Koehler 1) are plotted in the same figure (curve c)). In our measurements the resistivity increment corresponding to the same vacancy concentration at 100 °C is about seven times larger than in quenching experiments, and the activation energy is substantially lower.

Since we know the temperature dependence of $_T$, we could calculate $_T$ for the straight part of the curve (a) (Fig.2), but this can ot be used at higher temperatures. *)

Footnote: *) α is constant up to 500 °C, $_T$ steadily rises and therfore decreases with the temperature, though Grüneisen theory supposed to be constant. Similar disagreement was found in checking the validity of the relation $R_T T$ $_T$. In the temperature range from 500 to 1000 °C the value of ($_T \cdot T/R_T$) is constant within about 10% only.

We must therefore look for another method of extrapolating the second term in (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

$$\frac{d}{dT}(\ln\ ) = -\frac{1}{V}\frac{dV}{dT}\frac{d\ln}{d\ln V} = - \quad . \qquad (2)$$

Knowing the temperature dependence of the Debye temperature, we could determine α and thus the slope of log($_T$ 1) in $\ln \alpha$ beyond the linear region, but we have found no measurements of Θ (T) for gold. Moreover it is not certain whether the precision of these measurements performed usually by X-ray method would be sufficient for our purposes.

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

$$_T / \ _r = (V_r / V_T) = (a_r / a_T)^3 \qquad (3)$$

holds. $_T$, 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 T_r. In this approximation the Grüneisen constant is supposed to be constant and equal to 3 . (The highest value of in our measurements is 2,8). Using the lattice parameter expansion data of Simmons and Balluffi 8) we have plotted the temperature dependence of log $_T$ in Fig. 4. As reference Debye temperature T_r = 136 °K taken from

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Caption to Fig. 4.

Fig. 4. Temperature dependence of log , derived for = 3.

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12) was chosen. The points lie till 500 °C on a straight line, the slope of which gives 2 = 2,7 x 10^{-4}. This value is in agreement with the value 2,3 x 10^{-4}, derived from resistivity measurements. 2 is increasing at temperatures above 500 °C. We have thus obtained the temperature dependence of (2)' by supposing originally that is constant. Now we suppose that the slope of the true lattice resistivity curve should change in the same proportion as (2)' in Fig. 4 does. Then starting at the end of the straight interval of the curve (a) in Fig. . we may plot the curve (c), representing the lattice resistivity. The resistivity increment measure. from this curve leads to the acti-

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vation energy E_f = [illegible] ev, which is closer to the well established formation energy values derived from quenching experiments.

In constrary to this an other 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 defect and lattice resistivities. Then by subracting the computed resistivity of equilibrium vacancies (1,5 μ cm per at.% vac.) from the experimental curve the true lattice resistivity will be obtained.

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 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 expetiments of Lauerle and Koehler 1) 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

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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 u cm) at. % of vacancies. Also the activation energy E_v = 0.80 ev is nearer to the true value, slightly lower than 1 ev. In fact, without an improved theory any extrapolation will be a little speculative. Improved theory and higher accuracy in resistivity measurements may help to solve this problem.

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REFERENCES

1) J.E. Bauerle and J.S. Koehler: Phys.Rev. 107 (1957) 1493

2) F.J. Bradshaw and S. Pearson: Phil.Mag. 4 (1957) 379

3) W. De Sorbo: Phys.Rev. 117 (1960) 444

4) C.J. Meechan and R.R. Eggleston: Acta Met. 2 (1954),680

5) S.D. Gercriken and B.F. Sliusar: Ukrainian Phys.J. 2 (1957)376

6) S.D. Gercriken: Ukrainian Phys.J. 1 (1956), 193

7) J. Takamura: Acta Met. 9 (1961) 547

8) R.O. Simmons and R.W. Balluffi: Phys. Rev. 125 (1962),862

9) J.F. Nicholas: Acta Met. 3 (1955) 411

10) R.O. Simmons and R.W. Balluffi Phys.Rev. 117 (1960) 62

11) N.F. Mott and H. Jones: Theory of the properties of metals and alloys (Oxford University Press, 1936)

12) F.H. Herbstein: Phil.Mag.Supplement 10 (1961) 313

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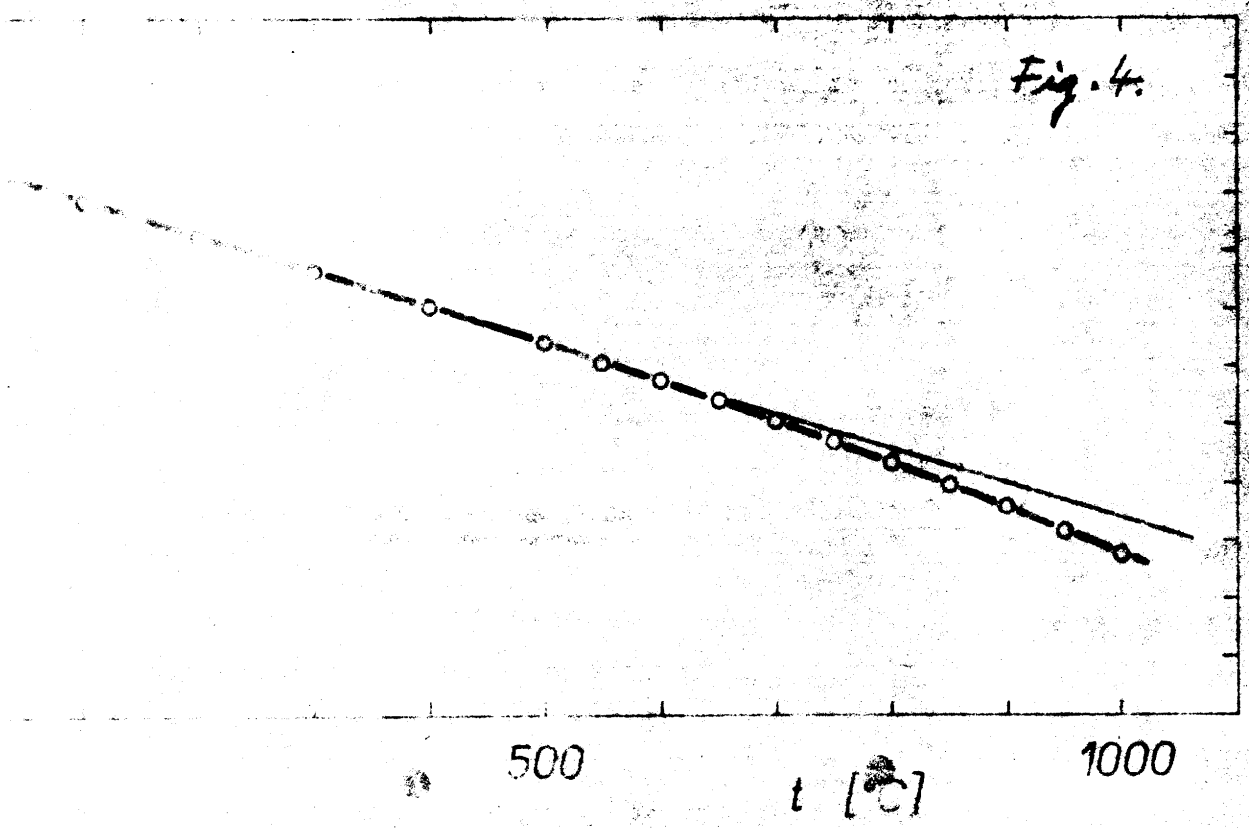

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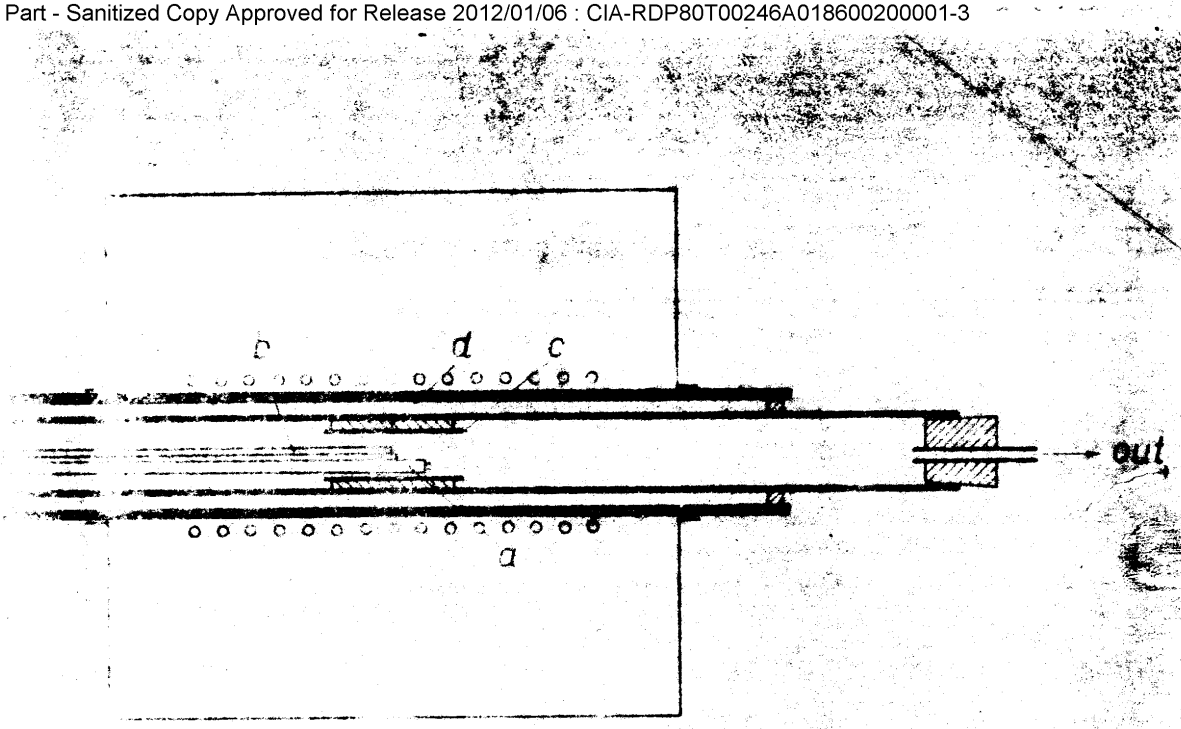
Fig. 1.



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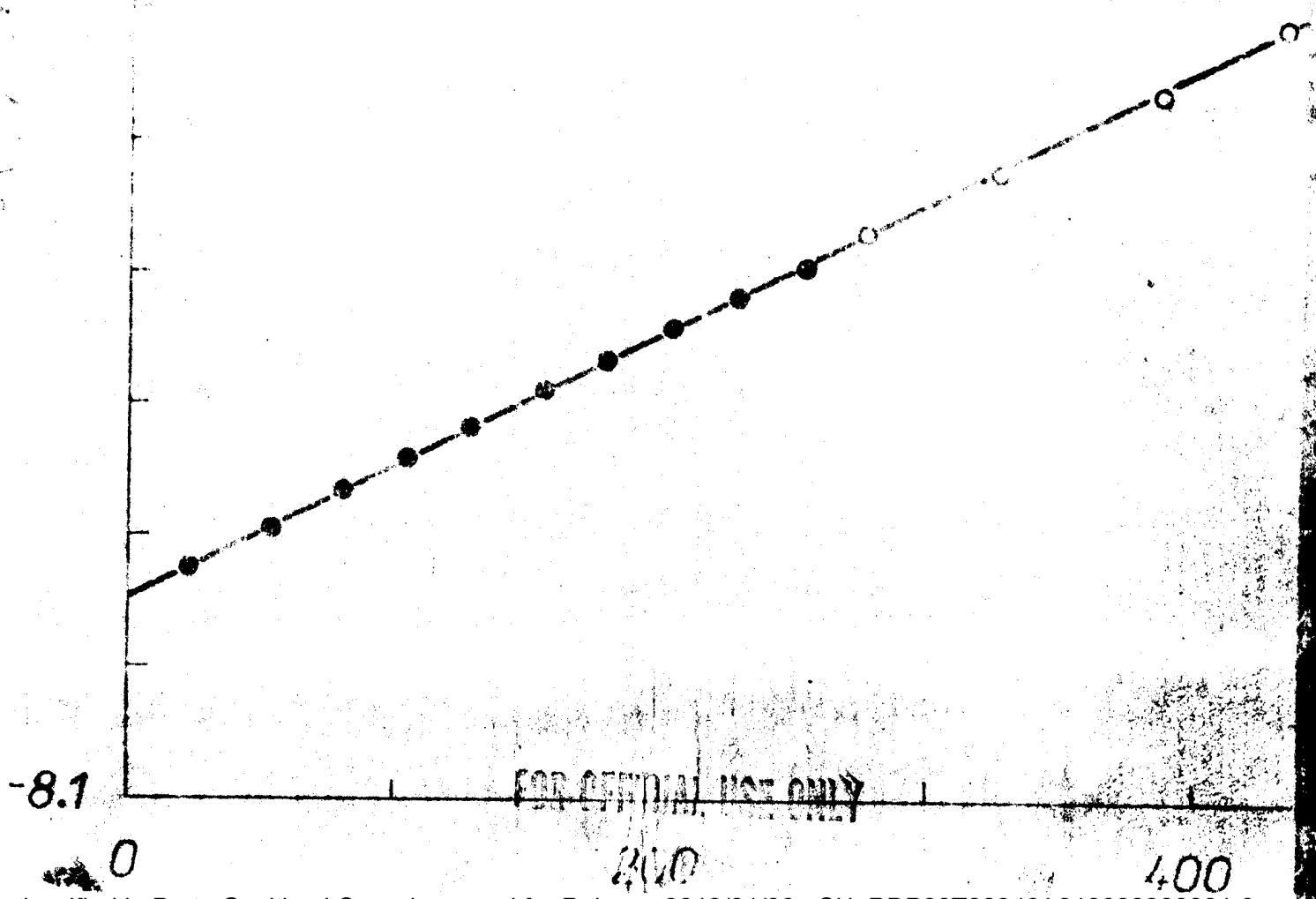

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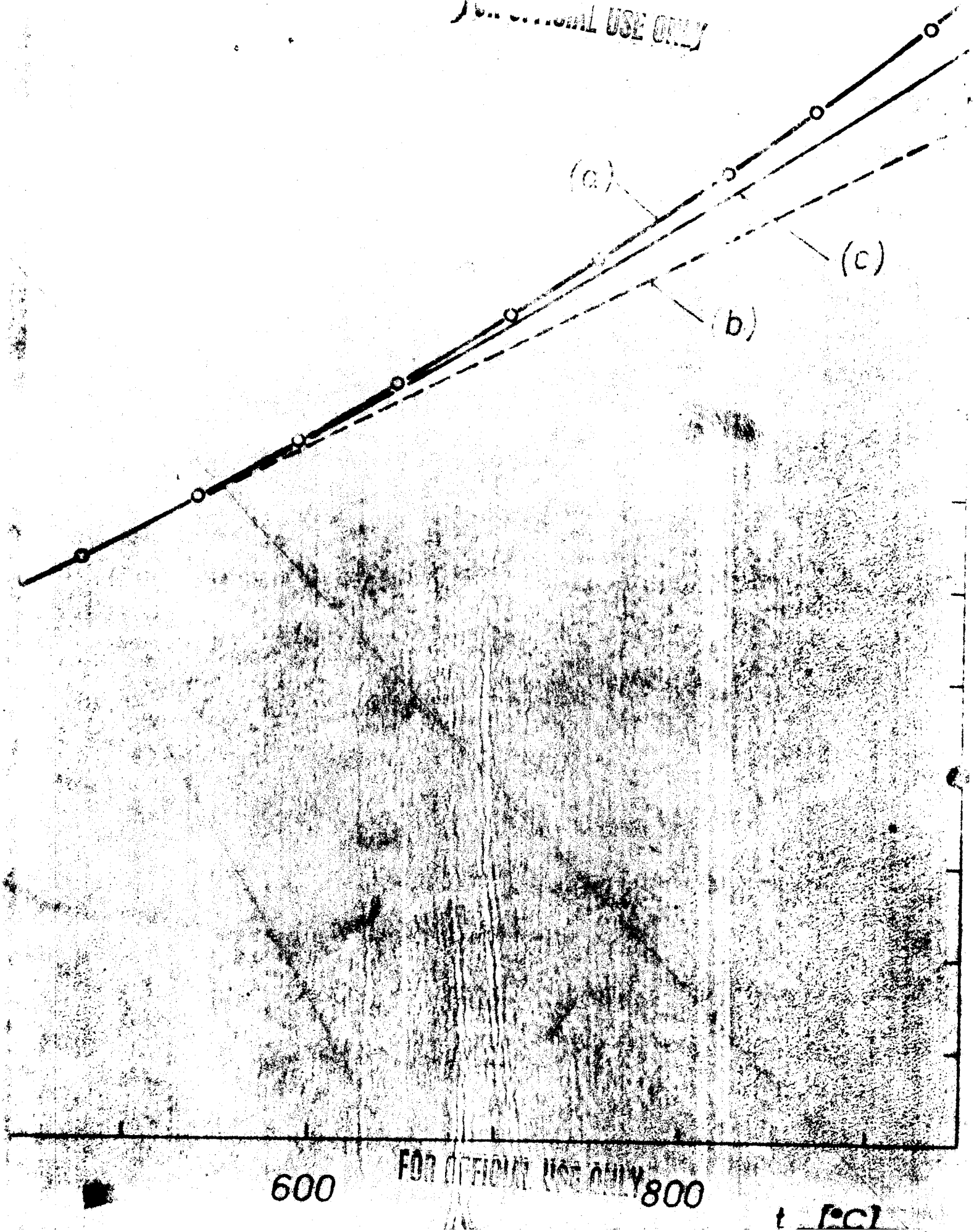

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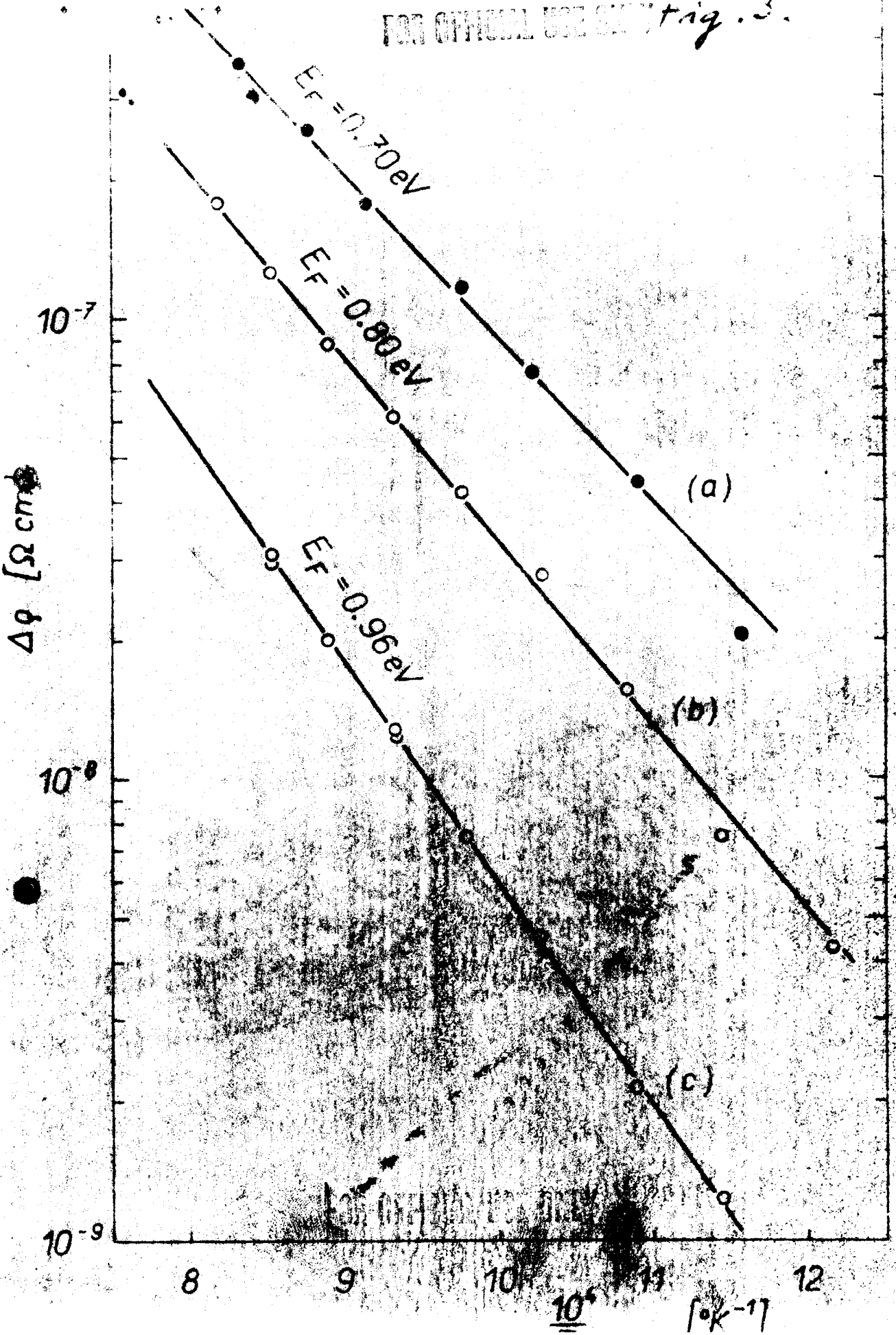
Fig. 3.



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