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MAGNETIC SUSCEPTIBILITY AND NEUTRON DIFFRACTION INVESTIGATION OF α-^{242}Pu

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ABSTRACT

Magnetic susceptibility and neutron diffraction measurements have been made on a high purity, polycrystalline sample of α-phase ^{242}Pu. The susceptibility results show the existence of weak ferromagnetism below 50°K. This suggests that the α-phase is antiferromagnetic, the observed ferromagnetic moment (9.5×10^{-4} emu per gram of sample at 4.35°K) originating within antiferromagnetic domain walls. No evidence for antiferromagnetic ordering was observed in the neutron diffraction study suggesting that the moment per Pu atom is too small to observe with this technique.

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The question of the existence of a magnetically ordered state in the alpha phase of plutonium at low temperature has been a subject of much interest and conjecture for some years.[1-3] Rocher and Friedel[4] put forth the hypothesis that α-Pu is antiferromagnetic with a Néel temperature around 100°K in an attempt to explain the observed low temperature resistivity anomaly in terms of spin-disorder scattering of the conduction electrons. Smoluchowski,[5] however, has proposed a band structure that can account for the resistivity anomaly in terms of interband scattering. Many physical properties of α-Pu have been measured[1-3] in attempts to substantiate the magnetic ordering hypothesis. Numerous anomalies have been observed and conflicting results on the same property by different investigators have been reported. Some of the measurements suggest magnetic ordering does occur, while others appear to refute it. The most direct and unambiguous way to determine if a substance is antiferromagnetic or not is by means of neutron diffraction. The available samples of plutonium up to now, however, have had much too large an effective absorption cross section and were too highly radioactive for good diffraction patterns to be obtained.[6]

Some of the anomalies reported in earlier work (e.g., specific heat) are now known to arise from self-induced radiation damage. A relatively large amount of high purity, electrorefined ^{242}Pu has recently been prepared under the auspices of the U.S.A.E.C. Transplutonium Program and the U.S.A.E.C. Isotopes Section. Plutonium samples are therefore now available in which the radiation damage is a minimum. Due to the relatively low effective absorption cross section of this isotope, neutron diffraction becomes feasible. We have made

neutron diffraction and magnetic susceptibility measurements on a polycrystalline rod of this material in the α-phase. The rod was 9.182 cm in length, weighed 48.47 g, its density[7] was 20.03 g/cm^3 and it had a calculated average diameter of 0.5779 cm.

The isotopic composition of the sample was reported[8] as 99.91 atom % ^{242}Pu with ^{239}Pu the largest isotopic impurity at 0.082 atom %. The isotopes ^{241}Pu, ^{240}Pu, ^{238}Pu and ^{236}Pu were present in the amounts 0.002, 0.011, 0.00043 and $\leq 3 \times 10^{-9}$ atom %, respectively. The chemical purity was reported[8] as 99.98% Pu. The principal impurities were Mg, Si, Fe, Cu and C which were present in the amounts of 15, 10, 8, 9 and <25 ppm (weight basis), respectively. The self-heating rate[9] was reported to be 11.73 milliwatts/100 grams.

Neutron diffraction powder patterns were obtained at room temperature, 145°, 80°, 35°, 20° and 4.2° K employing a variable temperature cryostat[10] on the powder diffractometer at the Livermore Pool Type Reactor. For these measurements, the sample was sealed in a thin-walled vanadium can with one atmosphere of helium exchange gas. No superlattice lines were observed at any of the above temperatures nor were any crystal structure changes observed. The observed patterns agree with the structure reported by Zachariasen[11] for the α-phase. A detailed account of these diffraction measurements will be given elsewhere but we can conclude here that no simple form of antiferromagnetic ordering occurs in α-Pu with a moment per Pu atom greater than about 0.5 Bohr magnetons.

As previously reported measurements of the magnetic susceptibility[12] showed little if any temperature dependence, and since we could detect no indications of antiferromagnetic ordering in the neutron diffraction measurements, we decided to attempt a careful examination of the susceptibility to high precision. The sample was the same as used in the diffraction measurements except that it was sealed in a thin-walled aluminum container with an atmosphere of helium exchange gas. The measurements were made with a magnetic force balance[13] consisting of a recording, semi-microbalance capable of weighing to ± 0.00002 g and a 6" electromagnet with field regulation and stability held to 1 ppm by means of a Hall probe regulator. The Gouy method was employed because of the geometry and polycrystalline nature of the sample. The mass susceptibility of a cylindrical rod of cross-sectional area A as determined by the Gouy method is given by[14]

$$\chi = 2g\Delta w/[\rho A(H^2-H_o^2)] \qquad (1)$$

where g is the acceleration of gravity, Δw is the change in sample weight in grams when the external magnetic field is applied, ρ is the density of the rod, and H and H_o are the values of the field at the two extremities of the rod. The fields H were determined with a nuclear magnetic resonance gaussmeter and the much weaker fields, H_o, were measured with a rotating coil gaussmeter. The precision to which χ is determined depends on the precision of Δw and $H^2-H_o^2$. The reproducibility of the H's was measured with the NMR gaussmeter and found to be 0.01%. The Δw values (of which, 0.30000 g is typical) are determined to about 0.01%. We estimate the

precision of χ then to be about 0.04%. We obtained an experimental indication of the precision from seventeen measurements of χ at room temperature (295.0 °K to 297.2 °K) in various fields from 4 to 8 kG. The measurements were spaced out over an interval of about three weeks with considerable temperature and field cycling between measurements. Assuming the temperature variation of χ is negligible between 295.0 and 297.2 °K we obtain an average value of

$$\chi_{AV}\ (296 \pm 1\ ^{\circ}\mathrm{K}) = (2.2604 \pm 0.0010) \times 10^{-6}\ \mathrm{emu/g}$$

where the uncertainty here is the standard deviation. This uncertainty is in reasonable agreement with the estimated precision of 0.04%. The above value of χ_{AV} has been corrected for the susceptibility of the aluminum sample container.

A variable temperature cryostat, which will be described in detail elsewhere,[15] allowed χ measurements to be made from about 4 °K to room temperature. In this cryostat, the sample is in thermal contact with a surrounding cylindrical heat exchanger via helium gas. The temperature of the exchanger can be varied by varying the flow of cold helium gas or liquid through it. The temperature is measured by a germanium sensor soldered to the heat exchanger. This sensor was calibrated in place against another germanium sensor suspended in the sample position. The sensor was easily readable to 0.1 °K but the uncertainty in the sample temperature at low temperatures, however, could be as much as 2 or 3 °K because of thermal gradients.

The field dependence of any susceptibility measurement should be determined as it has been shown that if a small ferromagnetic component is present in the sample the Gouy method gives[16]

$$\chi_H = \chi_\infty + 2\sigma/H \qquad (2)$$

where χ_H is the susceptibility measured in the field H, χ_∞ is the susceptibility at very large fields and σ is the saturation magnetic moment of the ferromagnetic component per gram of sample. We have made field dependent measurements at a number of temperatures between 4°K and room temperature on both the empty aluminum sample holder and on the holder plus Pu sample. Four typical χ_H vs 1/H plots are shown in Fig. 1. All values have been corrected for the sample holder and are thus for Pu alone. The field independence shown by the 294.7° and 57.0°K plots was observed for all temperatures examined between about 50°K and room temperature. Below this temperature, field dependence was observed. The "true" paramagnetic susceptibilities, χ_∞, obtained by linear extrapolation to infinite field, are seen to increase by only about 2% between room temperature and 4.35°K. The χ_H-values obtained at 4.35°K depend on the magnitude of the external applied magnetic field during cool down. It is interesting to note that the "true" paramagnetic susceptibility, χ_∞, at 4.35°K is independent of the value of the field applied during cool down.

The temperature dependence of χ_∞ and χ_H for H = 4 and 7 kG is shown in Fig. 2. The curves below 50°K are warming curves. The sample was first cooled to 4.35°K in an applied field of 14 kG. The external

field was maintained at 14 kG throughout the warming runs except for the few minutes it took to make the Δw measurements at 4 and 7 kG. The 4 and 7 kG curves in Fig. 2 are composites of two independent runs and illustrate the reproducibility of the data. To obtain reproducible results it was found necessary to start from above 50°K each time, cool down to 4.35°K in some applied field and then to measure χ on warming with the cool-down field applied to the sample between measurements.

The values of σ, as determined from the slope of the χ_H vs H^{-1} curves, is shown plotted against temperature in Fig. 3. The solid curve is associated with the measurements of χ_H in which a 14 kG field was applied as described above. The results of two independent runs are clearly indicated in this figure. Also indicated are the values of σ obtained at 4.35°K upon cooling down through 50°K with applied fields ranging from 0 to 10 kG.

It is clearly evident in both Figures 2 and 3 that a magnetic transition of some kind is occuring at about 50°K. We have considered three possibilities to account for this behavior: (1) the presence of a ferromagnetic impurity in small concentration, (2) intrinsic ferromagnetism of plutonium and (3) antiferromagnetism. Even though our material is of high chemical purity, it is difficult to absolutely rule out impurities as the source of the magnetic behavior. However, no known compounds of plutonium exhibit magnetic ordering around 50°K to our knowledge. We checked for sample homogeneity by displacing the sample vertically 0.835 cm with respect to the magnet and remeasuring σ at 4.35°K. The values of σ

before and after the displacement agree to within 0.1% indicating that the observed magnetic behavior is not due to some localized magnetic inclusion or granule.

If α-Pu is intrinsically ferromagnetic, with a Curie temperature of about 50°K, then the calculated moment per Pu atom is about 10^{-4} Bohr magnetons. We have little feeling for the possible existence of such a weak ferromagnetic state. If, however, α-Pu is antiferromagnetic with a moment per atom of about 0.3 Bohr magnetons as postulated by Rocher and Friedel,[4] then it is possible that below 50°K we are observing a net magnetic moment associated with antiferromagnetic domain boundaries as discussed by Li[17] and suggested as the source of the weak ferromagnetism observed in α-Mn.[18] If this is the case, then the field dependent behavior of σ at 4.35°K becomes more easily understandable as the net moments in the antiferromagnetic domain boundaries tend to line up with the applied field. The larger the applied field the better this alignment will be and thus the greater the measured σ. The small value of σ would also be understandable as only a small percentage of the Pu atoms would be involved in the domain boundaries. Our negative neutron diffraction results do not conflict with this interpretation. The crystal structure of the α-phase is complicated and numerous lines are obtained in the diffraction pattern which makes it difficult to see a moment of the size suggested by Rocher.

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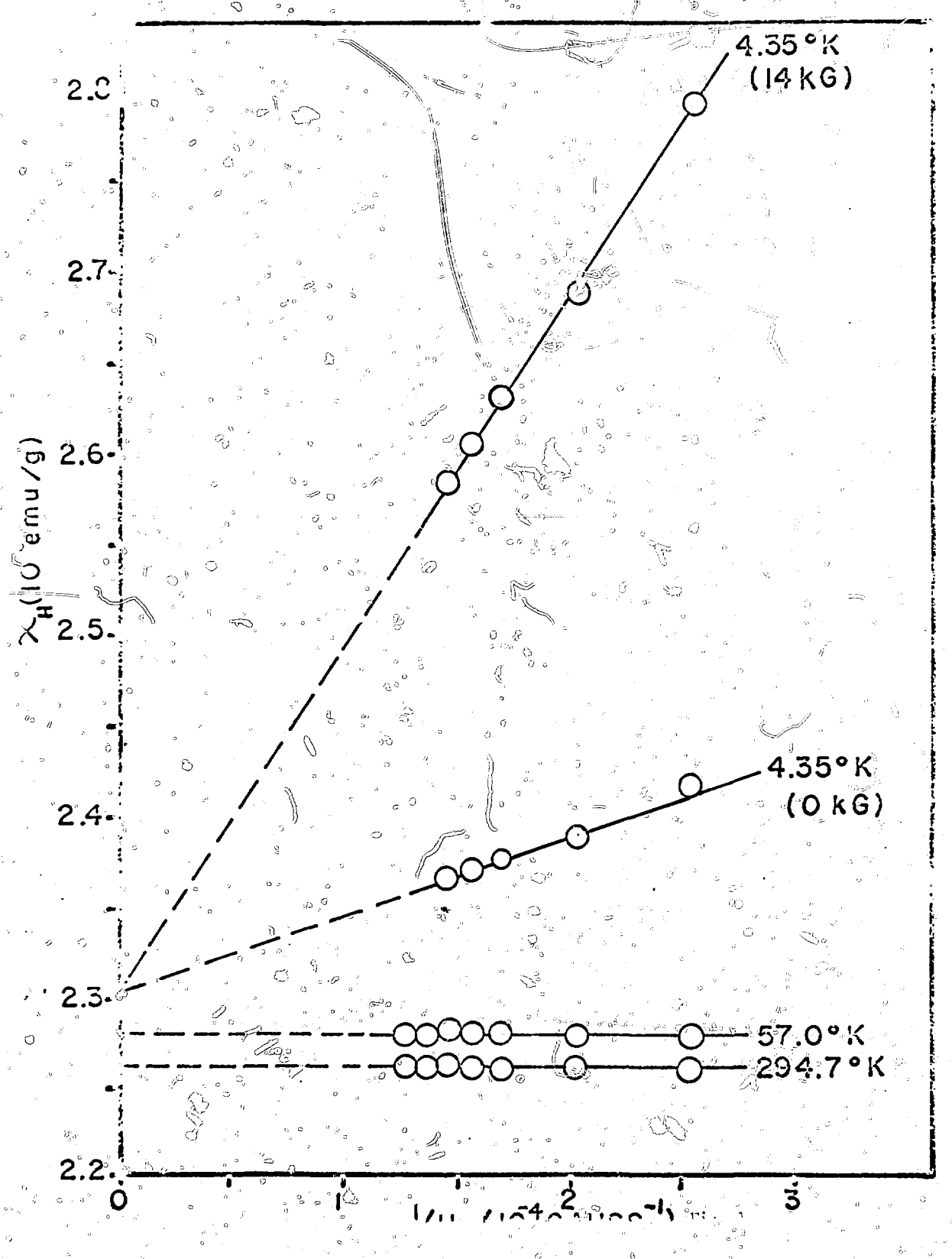
FIGURE CAPTIONS

Fig. 1 Magnetic susceptibility as a function of H^{-1}. The labels 14 and 0 kG on the 4.35°K curves refer to the value of the applied external field on cooling to 4.35°K.

Fig. 2 Magnetic susceptibility measured at H = 4 and 7 kG as a function of T. These are warming curves obtained after first cooling to 4.35°K in an external field of 14 kG. The χ_∞ curve is obtained by linear extrapolation of χ_H vs H^{-1} curves to infinite field. The solid circles indicate field independent points.

Fig. 3 The ferromagnetic moment, determined from the slope of χ_H vs H^{-1} curves, as a function of temperature. The numbers on the points at 4.35°K refer to the value of the external field (in kG) applied during the cool down to 4.35°K. The circles and triangles are the results of two independent warming runs.


4.35°K
(14 kG)
4.35°K
(0 kG)
57.0°K
294.7°K
χ_H(10^{-5}emu/g)
2.8
2.7
2.6
2.5
2.4
2.3
2.2
0
1
2
3

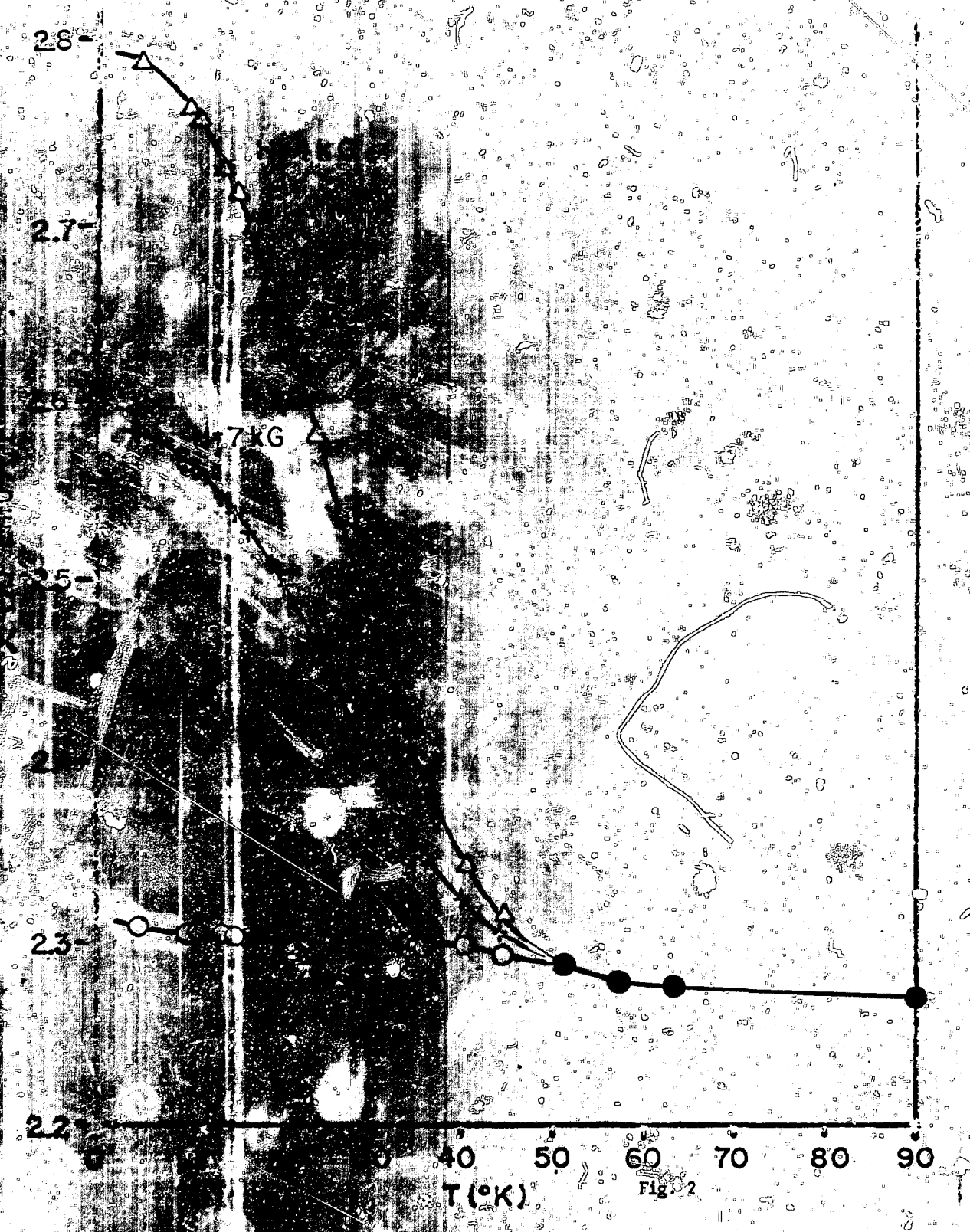


Fig. 2

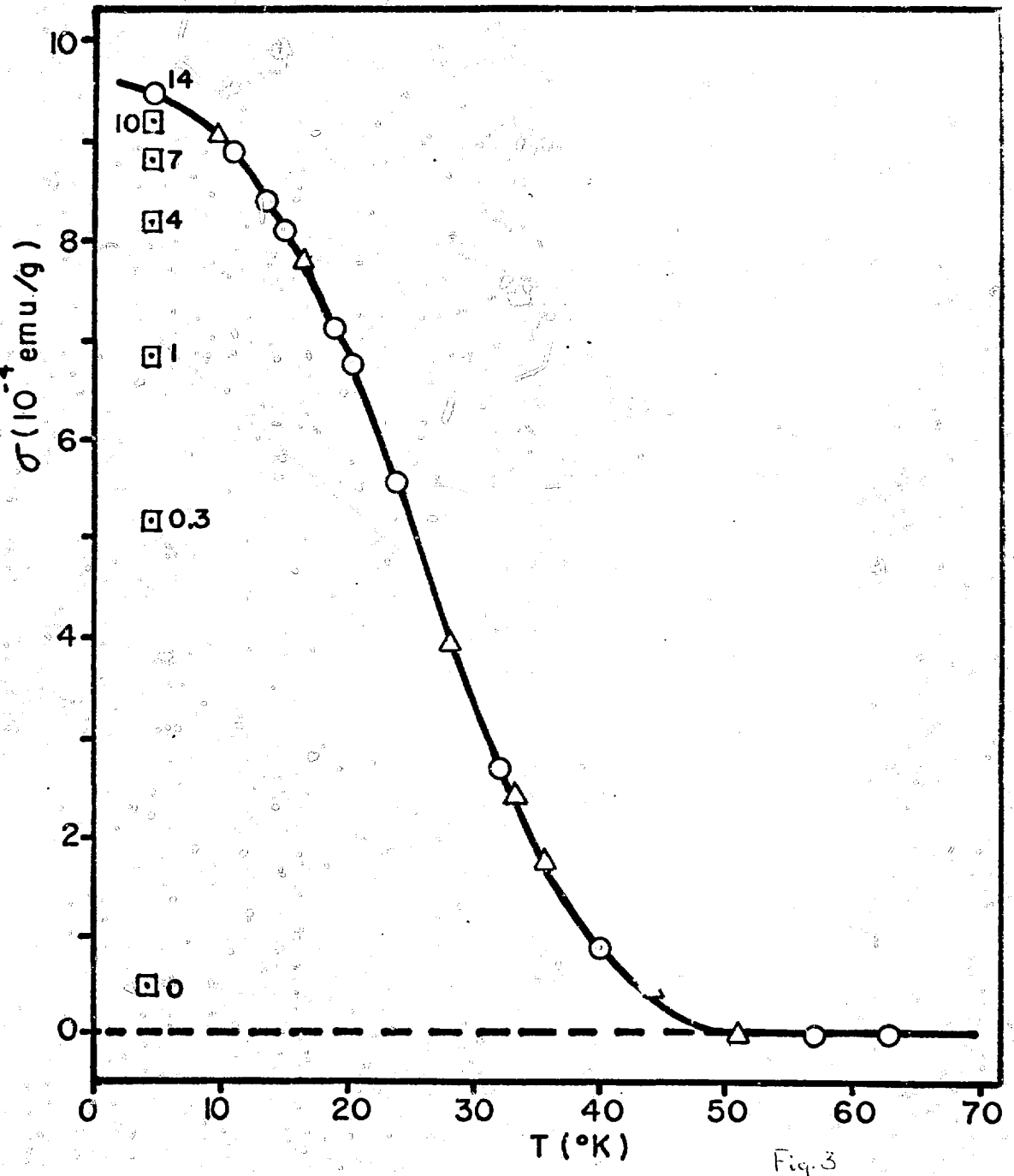


Fig. 3