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ABSTRACT

The electrical resistance of dysprosium is examined carefully in the temperature-pressure range 77° to 200°K and 15 to 120 kbars. Room temperature isotherms are also included. The variation of the Néel transition with pressure was found to good accuracy: the value of dT_N/dP is -0.62 ± 0.04 deg/kbar. Using this result, second order thermodynamic equations yield values of -64×10^{-6} $(°C)^{-1}$ and 4.0×10^{-14} cm^2/dyne for the changes in the coefficient of linear expansion and the compressibility respectively at the one atmosphere Néel point. The Néel transition disappears in the region 45-55 kbars, and no magnetic transitions are seen at higher pressures in the temperature range indicated. The other boundaries in the region investigated have been determined but are very uncertain. Above the Néel line, dT/dP is very large and the sign of its slope is undetermined. Below the Néel line, dT/dP has a value in the range -1 to -4 deg/kbar. This transition, which occurs at room temperature in the range 46 to 52 kbars, could be either first or second order.

The unfilled 4f shell of dysprosium gives rise to its magnetic properties. Below 85° K at one atmosphere, dysprosium is ferromagnetic; between 85° and 178.5° K, it is antiferromagnetic; and above 178.5 °K it is paramagnetic (1). Neutron diffraction (2) shows the antiferromagnetic structure to consist of ferromagnetic sheets perpendicular to the c-axis of the hexagonal close-packed structure. The moments of these sheets spiral as one moves along the c-axis. The turn angle between one plane and the next is 26.5° at the Néel point and 43.2° at the Curie point.

The Néel transition is second order, as confirmed by the continuity of the lattice parameters at the transition point (3). In the paramagnetic state, both lattice parameters, a and c, decrease as expected with decreasing temperature. Below the Néel point, a continues to decrease but c increases as a result of the magnetic forces coming into play in the antiferromagnetic state.

The Néel point of dysprosium is easily seen in the resistivity-temperature graph, as shown by the 40 kbar isobar in Fig. 1. The Néel point is particularly well marked by the change in the slope of the resistivity-temperature curve at that point along with a small resistivity peak. Most of the observed resistivity is due to spin-disorder scattering (4), which arises from the interaction of the conduction electrons with any disordered spins on lattice sites. This spin disorder increases with temperature until complete randomness occurs in the paramagnetic state. Hence the spin disorder and the observed resistivity level off above the Néel point. The resistivity peak at the Néel point (as well as the rise at the Curie point) are caused by a small additional contribution to the resistivity by the antiferromagnetic state. Single crystal work (5) indicates that this antiferromagnetic state contribution to the resistivity is a maximum for current moving along the c-axis and vanishes along the a-axis. The added resistivity is due to the periodic spin structure along the c-axis (6).

In the resistivity-pressure curve of dysprosium, Bridgman (7) found a shoulder at about 70 kbars. A correction of his pressure scale yields a true value in the range 52-55 kbars. Stephens and Stromberg (8) obtain a room temperature value of 52±1 kbars. This shoulder may be seen in the isotherms in Fig. 2.

The ferro-antiferromagnetic Curie transition has been examined by Swenson under pressure, yielding a value of dT_c/dP of -1 deg/kbar (9). The highest pressure attained does not seem to have been higher than a few kbars.

Spectral analysis of the dysprosium (10) showed 0.1% Al, 0.1% Ca, and 0.04% Mg. The aluminum and magnesium were probably present as impurities in the hydrochloric acid that was used to dissolve the dysprosium before plating onto the electrodes.

The dysprosium was too hard and brittle to be extruded into a wire. The 3-1/2 mil foil was cut with a razor into strips 1/2 x 0.004 inch in size. Each hoop was bent into a hoop and then pressed to about 1-1/2 mils thickness. The edges of each hoop were pared with a knife until the width was about 8 mils. These hoops were then annealed by heating to 800°C in a high vacuum with slow cooling. The hoops were allowed to slowly cool to room temperature while still under vacuum. The hard oxide film was scraped off to provide adequate electrical contact.

The Bridgman anvils and the mounting of the samples have been described elsewhere (11). The silver chloride discs in the sample were covered with clear acrylate paint to prevent reaction with the dysprosium. Final assembly of the sample was done in a dry atmosphere to prevent moisture absorbed by the deliquescent dysprosium chloride from accelerating the dysprosium-silver chloride reaction. The sample was sealed at the edges with acrylate paint to maintain dry air near the hoop until compressed.

The temperature-pressure region between 77° and 200°K and between 15 and 120 kbars was covered with both isobars and isotherms. The measurement techniques for pressure, temperature, and resistance, as well as pressure calibration, have been discussed elsewhere (12). Room temperature pressure calibration was used at all temperatures. The isobars were taken using heavy copper blocks previously described (13). In both heating and cooling, the temperature was changed at a slow rate of about 0.3 degree per minute. These measurements were made slowly in order to obtain the resistivity peak at the Néel point, which does not appear if the temperature is changed too quickly. The temperature difference between the thermocouples above and below the sample was two degrees or less. At each pressure on a given sample, the heating and cooling measurements gave the same value of the Néel point to within a degree. Two week-long sets of isobars were taken with different samples.

Several isotherms were run. Bare anvils were used at room temperature, 195°, and 77°K with the appropriate baths being used. A single experiment was conducted at 125°K using the copper blocks. These experiments were shorter than the isobar measurements, for the range to 100 kbars was covered in only a few hours.

Several of the resistivity-temperature curves for the isobaric experiments are shown in Fig. 1, which covers a narrow temperature range about the Néel points. Three regions of behavior are represented in this figure. From 15 to 45 kbars, the resistivity peak at the Néel point, although small, is readily visible. At 50 and 55 kbars, the Néel point is poorly defined.

Although the change of slope is still present, the resistivity peak has disappeared. As estimated from measurements below 50 kbars, about six degrees must be added to the change-of-slope temperature to give the true Néel temperature at the top of the resistivity peak. In the range 60 to 120 kbars, the Néel transition has disappeared. No magnetic transitions were seen between 77° and 200°K in this pressure range. Instead, the resistivity is nearly linear with temperature. The phenomenon associated with the resistivity shoulder does not appear in the isobars. The results of the isobaric measurements may be plotted so as to yield isotherms. These derived isotherms, some of which are shown in Fig. 2, yield phase lines for the phenomenon represented by the resistivity shoulder. In both Figs. 1 and 2, the measured electrical resistance has been converted to resistivity using 92 micro-ohm-cm as the room temperature, one atmosphere resistivity of polycrystalline dysprosium (14). Bridgman's (7) room temperature resistances at one atmosphere and 15 kbars were also used.

All the results are shown in the phase diagram in Fig. 3. The Néel point measurements were the best taken in this experiment and the Néel line is well defined. The Néel temperature drops with increasing pressure. The value of dT_N/dP is -0.62±0.04 deg/kbar. At pressures above 45 kbars, the Néel line begins to disappear as mentioned above. In contrast to the Néel line, the phase lines of the shoulder phenomenon are very poorly defined. The pressures at a given temperature are all higher for the isothermal than for the isobaric experiments. In Fig. 3, phase lines have been drawn through both the isobaric and isothermal points. Above the Néel line, dT/dP is very large according to either type of experiment. The direction of the slant of this line cannot be determined. Below the Néel line, dT/dP varies from -1 toto-4 deg/kbar depending on whether isobaric or isothermal values are examined.

The Néel line seems to disappear in the region where the shoulder phase line occurs.

An attempt was made to equilibrate the dysprosium by pulsing two amperes of current through for a fraction of a second, thus heating and annealing the sample. One such experiment yielded a room temperature shoulder pressure of 43 kbars. However, this technique is not developed enough to yield reliable values.

The phenomenon associated with the resistivity shoulder seems to be extremely sluggish. At a given temperature, lower pressure values for the shoulder are obtained in the week long isobaric experiments than in the isothermal measurements covering a few hours. At room temperature, the isobaric shoulder pressures seem to be fairly reproducible in the region of 46 kbars. Similarly, the isothermal pressures cluster about 52 kbars, in agreement with Stephens and Stromberg. Probably the lower value is closer to the true equilibrium pressure, since the dysprosium is presumably better equilibrated.

The 15 and 20 kbar isobars were carefully measured in the temperature region above 77°K, but the Curie transition was not found. This confirms Swenson's report (9) that the Curie temperature decreases with pressure.

Two new properties of dysprosium may now be calculated using the Clausius-Clapeyron type equations for second order transitions (15). At the Néel point:

$$\frac{dT}{dP} = \frac{TV\,\Delta\alpha}{\Delta C_p} \qquad \frac{dT}{dP} = \frac{\Delta\beta}{\Delta\alpha}$$

where $\Delta\alpha$, $\Delta\beta$, and ΔC_p are the changes in the coefficient of linear expansion, compressibility, and heat capacity at constant pressure, respectively. The values for the one atmosphere Neel point are -0.62 deg/kbar and 8.5 cal/deg-mole (16) for dT_N/dP and ΔC_p respectively. Values of $\Delta\alpha$ and $\Delta\beta$ are calculated to be -64×10^{-6} $(°C)^{-1}$ and 4.0×10^{-14} cm^2/dyne respectively. By way of comparison, α is 8.5×10^{-6} $(°C)^{-1}$ near the Néel point (17) and β is 2.44 $\times 10^{-12}$ cm^2/dyne at room temperature (18). The same magnetic forces that cause the lattice parameter c to increase below the Néel temperature are probably related to the very large change in the coefficient of linear expansion.

The phenomenon associated with the resistivity shoulder may be called a transition since the magnetic properties of the dysprosium change. It is not possible to state the type of transition that occurs. Jamieson (19) has recently studied dysprosium and his pressure-volume work above 50 kbars does not extrapolate to Bridgman's work below 38 kbars (corrected). Jamieson's work indicates that there may be a 10 percent volume decrease in the region 40 to 50 kbars. However, his X-ray work shows the same hexagonal close-packed structure above 50 kbars. This transition might be a first order resembling that of cerium (20), in which there is a volume discontinuity but both the high and low pressure phases possess the same type of structure. In cerium, it is thought that a 4f electron is pushed into a 5d state, thereby reducing the volume of the cerium ion core and allowing shrinkage to a smaller volume. The situation in dysprosium may be similar, with partial or total removal of an electron from one state to another. It is also possible that such an electronic shift may occur, but that the volume decreases rapidly but continuously in the region 40 to 50 kbars. Such a transition would be second order. It is not possible, moreover, to guess the magnetic properties of the high pressure phase of dysprosium. It may be paramagnetic with a magnetic transition below 77°K. It may also be magnetically ordered with a Curie or Néel point above 200°K. Since at one atmosphere, a reduction in volume occurs upon cooling and magnetic ordering occurs, a reduction in volume by application of pressure might produce a similar result.

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FIGURE CAPTIONS

Figure 1 Several resistivity-temperature isobars for dysprosium over a narrow temperature range near the Néel points.

Figure 2 Some resistivity-pressure isotherms for dysprosium derived from the isobaric measurements. Triangles and circles refer to the two isobaric experiments.

Figure 3 Temperature-pressure phase diagram for dysprosium. Triangles and circles refer to the isobaric measurements. Squares refer to the isothermal experiments. The diamond is the one atmosphere value (1).

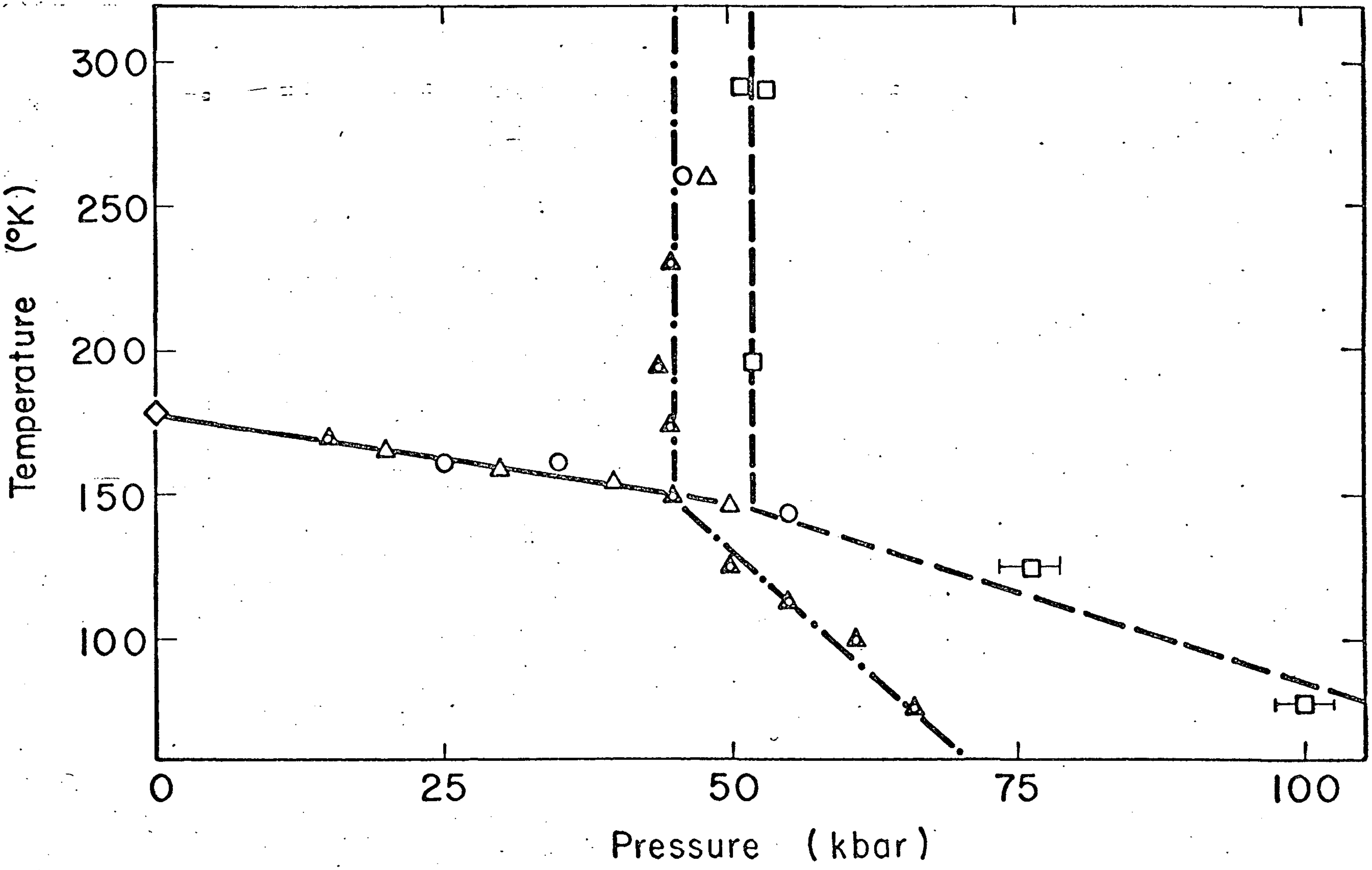

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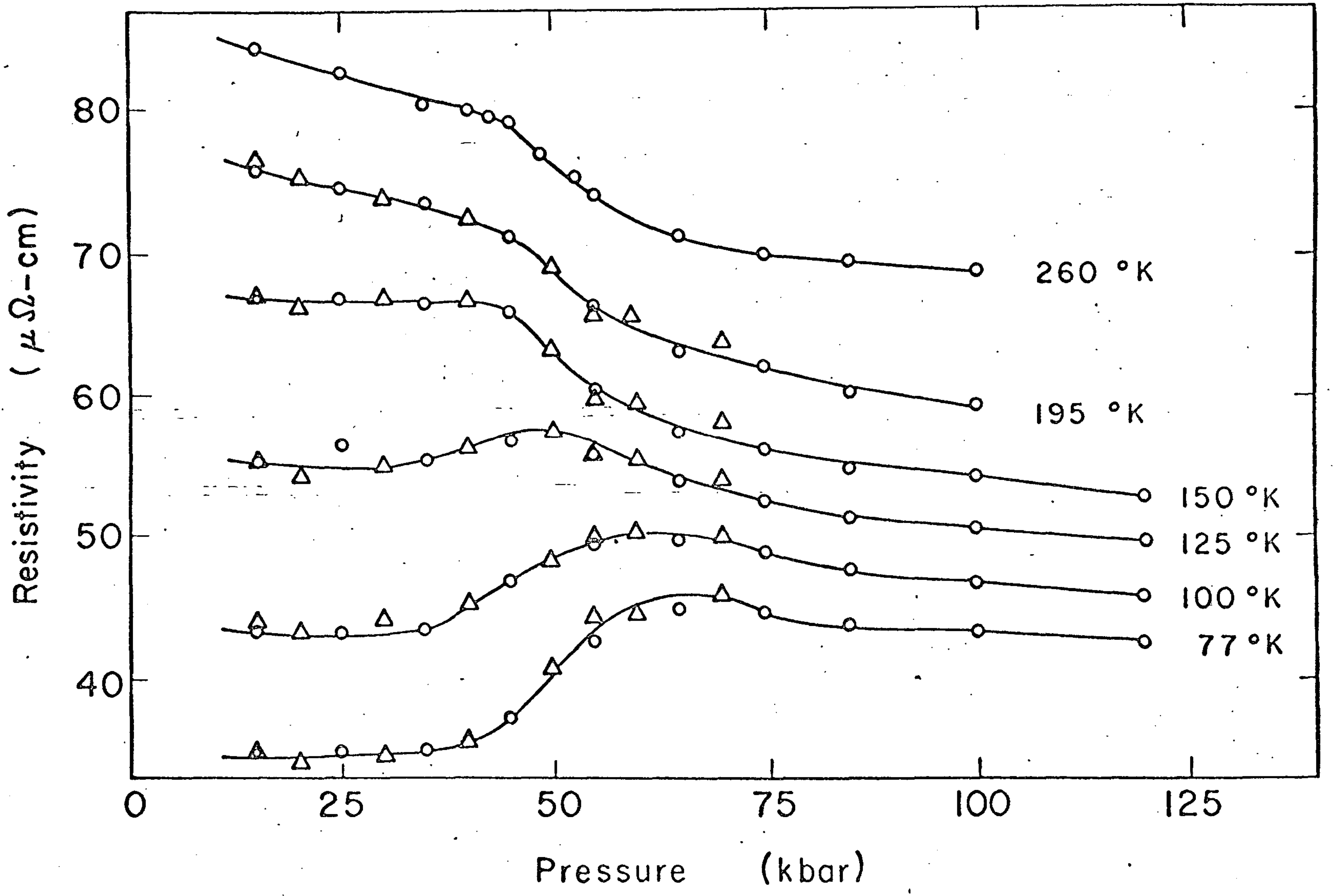
Fig. 1



MU-33131
Fig. 2

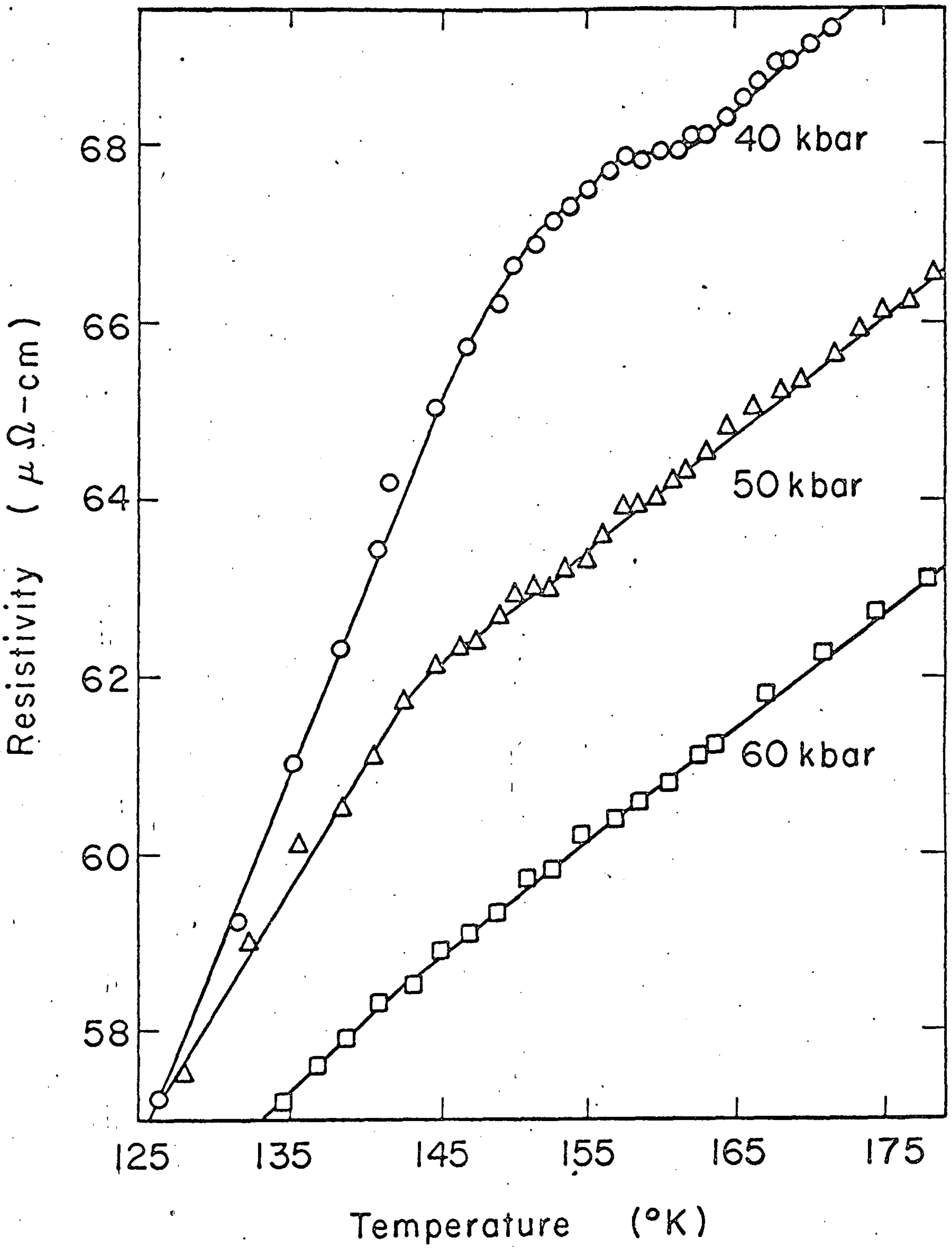


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Fig. 3