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SEMICONDUCTING REGION OF YTTERBIUM

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Abstract

The resistivity of elemental ytterbium at room temperature rises by a factor of eleven to a maximum at a pressure of 40 kbars; a further pressure increase causes a polymorphic transition; the new phase has a resistivity of 0.8 that of the 1 atmosphere value of the metal. In the T-P diagram, the phase boundry has a negative slope. The phase boundry has been determined from -190° to 360°C, and has been found to be a straight line that extrapolates reasonably close to the known α-β transition at one atmosphere. At pressures between the transition pressure and 20 kbars, the lowest pressure to which the measurements were made, the ytterbium exhibited a conductivity behavior that is typical of a semiconductor. The temperature coefficient of resistance is negative, and at constant pressure, the resistivity is accurately described by the usual exponential temperature dependence characteristic of a semiconductor. The parameter in the expontial would correspond to an energy gap of 0.015 ev at 20 kbars, an increase with pressure to a maximum of 0.080 ev at 37 kbars, and then a decrease to 0.05 ev at 45 kbars.

Introduction

In 1954 Bridgman (1) published the pressure-volume relationships to 39 kbars and the resistivity to a presumptive 98 kbars for a number of the rare earth metals. His pressure scale for the volume work is correct, but on the resistivity work, the scale he used is incorrect. In the following, his figures are corrected where possible to conform to a pressure scale based on the bismuth 1-2 and 6-8 transitions occuring at 25.5 and 88 kbars respectively. Particularly intriguing were the results on ytterbium. He found that at room temperature the resistance of ytterbium increased eleven-fold at a pressure of 40 kbars and then rapidly decreased to a value which was 79% of that at one atmosphere. This value remained nearly constant to about 80 kbars. Vereshchagin et al. (2) obtained similar results and found that the resistance beyond the peak remained level at least to 200 kbars. Our own work indicates a shallow minimum at about 80 kbars. Both Bridgman and Vereshchagin suggested that the resistance peak represented a polymorphic transition. Recently Hall and coworkers (3) verified that a phase change occurred, and the crystal structure changed from face centered cubic to body centered cubic. Such a change is known to occur at 1 atmosphere at a temperature of 798°C.

The large increase in the resistance of ytterbium was such that Bridgman investigated the temperature coefficient of resistance from 0° to 200°C at pressures from 1 atmosphere to 7 kbars. From 1 atmosphere through 6 kbars, the temperature coefficient of resistance was normal for a metal in that the resistance increased with the temperature. At 7 kbars, there was a decrease in resistance from 0° to 100°C, and then the resistance started to increase in the characteristic manner of a metal. He suggested that ytterbium was being squeezed into a semiconducting state. It is this

behavior that is the prime purpose of this investigation. The greatest care was taken at temperatures below room temperature. If there was an electrical behavior that was characteristic of semiconduction, it would be most pronounced at the lower temperatures. Unfortunately, our work cannot be made to join that of Bridgman since we were restricted to the pressure region above 20 kbars. In the region between 20 kbars and the α-β phase boundary, ytterbium exhibited electrical characteristics that were characteristic of semiconductors with respect to the magnitude of the resistivity and the temperature coefficient of resistance.

Experimental

The ytterbium used in this investigation was obtained from Research Chemicals, Phoenix, Arizona, and was supposedly 99.9% pure. Spectral analysis performed in this laboratory by Mr. George Shalimoff showed the following impurities: Al, 0.015%; Ca, 0.03%; Fe, 0.025% and Mg, 0.01%. All other elements were present in quantities less than those detectable by ordinary spectrographic analytical techniques. The metal was extruded into wire 0.003 inch in diameter, and annealed in an argon atmosphere for 15 minutes at 400°C.

The Bridgman anvils, silver chloride discs and pressure measurements have been described (4). The resistance of the sample was determined by measuring the voltage drop from the shoulders of the anvils. The current was obtained from a regulated constant current supply. The resistance of the anvils in direct contact was on the order of 30 micro ohms. There was also a contact resistance, but both these contributions to the resistance were negligible since the resistance of the sample was several ohms. Since

the readings were recorded, these factors were negligible to the accuracy of the measurements.

Above room temperature the entire anvil assembly was heated by a cylindrical furnace. In these determinations, there was a temperature gradient in the system. The true values of the resistance were obtained by averaging the readings obtained with the current flowing in opposite directions. The isothermal determinations at dry ice and liquid nitrogen temperatures were made in dry ice -isopropyl alcohol and liquid nitrogen baths. For the constant pressure runs, the system was immersed in a bath of Kanolt No. 40 solution (5). This system was quite fluid to temperatures as low as 140°K. Temperatures were determined with two copper-constantin thermocouples welded to the shoulders of the anvils, one above, the other below the sample. When there was a temperature difference, the average of the two readings was used. In these cases, the EMF readings were the averages of the results obtained with the current flowing in both directions. The thrust on the anvils was determined with a 200 ton strain gauge in conjunction with a Baldwin Lima SR4 bridge. The pressure on the sample is exactly known only at room temperature. It was assumed that the pressure gradient in the system was essentially zero at 400°C. The pressure gradient was assumed to be a linear function of the temperature. This is almost certainly incorrect, but by the proper choice of the hoop radius, the error is minimized. Actually, the pressures were sufficiently low in this investigation that these variations were not too great.

Results and Discussion

Figure 1 shows an isothermal determination of the resistance of ytterbium as a function of pressure at 20°C. This curve shows a sharp break in the resistance at 40 kbars, the α-β transition. To obtain this sharp drop, it is necessary to wait about two hours from the time the resistance starts to decrease until it becomes approximately constant. This is an exceedingly slow transition rate. On decompression, the reverse transition does not occur completely until the pressure has been completely removed for at least several minutes. Thus, there is some doubt as to what the equilibrium values for the transition are. In spite of the large barrier, the results on compression are highly reproducible. Since the observed transition pressures on compression extrapolate closely to the observed transition pressure at one atmosphere, it can be assumed that the values obtained on compression are either equilibrium values, or are not far removed from these values. Figure 2 exhibits some of the measured isotherms from 77°K to 600°K. The one atmosphere points are those of Spedding (6). The resistances of the curves at the various temperatures were determined from the 20°C and 20 kbar value given by Bridgman.

Of particular interest are the resistance-temperature determinations at constant pressure. Some of these results are shown in Fig. 3 where log R is plotted against 1/T. R is the resistance, and T the absolute temperature. It is immediately apparent that in all of these determinations the resistance behavior is that typical of a semiconductor and not that of a metal. Also it should be noted, that there is essentially little if any difference in the resistance value on heating or cooling.

The phase boundary can be obtained from the data of Fig. 2, and the result is shown in Fig. 4. The points were obtained on the assumption that the phase boundary was the pressure at which the resistance first started to decrease. At liquid nitrogen temperatures, attempts to obtain a sharp decrease in the resistance after the maximum failed. Even permitting the sample to stay at pressure for nearly a half an hour showed very little effect on the resistance at a given pressure. To wait for the resistance to decrease to its lowest values would have taken years at the rate at which the resistance was decreasing. This very slow decrease in resistance could be due to the fact that the transition occurs piece-wise at these low temperatures. It has been observed by us that frequently the bismuth 1-2 transition at -80°C occurs in steps. Some times three pressure increments are needed before the transition is complete. One would expect that the sluggishness of a transition would increase as the pressure is increased and the temperature is lowered.

Of greater interest is the nonmetallic behavior as shown in Fig. 3. The maximum observed resistance in the system was 0.013 ohm cm, a value much too high for any metal, and characteristic of a very heavily doped sample of germanium. The temperature coefficient supports the view that the material has become a semiconductor. If the energy gap is computed in the usual manner

$$R = Ae^{(Eg/2kT)}$$

the gap is found to be a strong function of the pressure. The results of the calculations are shown in Fig. 5. Since the purity of this material is only 99.8%, it is evident that this gap is not the intrinsic value, but

rather that of the impurity levels. On a highly purified sample, it would be expected that these gaps would be higher than that reported here.

Evidently there are some unexpected peculiarities in the electronic structure of ytterbium. First let us consider the values of the resistances involved. It is known that the rare earths have unusual magnetic properties. A perusal of the literature shows that no known magnetic change can account for the magnitude of the change observed here, a factor of nearly 800. Resonance scattering (7) of the electron between the 4f and 5d level again could not account for this very large increase.

The electronic configuration of ytterbium in the gas phase is $4f^{14}5s^{2}5p^{6}6s^{2}$. The magnetic susceptibility data of Lock indicate that in the solid only 1/250 of the 4f electrons are in the 5d state (8). This implies that the binding is through the $6s^{2}$ electrons, a binding similar to that of the alkaline earth metals. This latter is born out by the compressibility of ytterbium. Ytterbium, according to Bridgman's measurements, is much more compressible than the other rare earths he measured. In fact the compressibility of ytterbium is very close to that of barium. This means that the original conductivity is due to the overlap of the 6p and 6s bands.

If it is assumed that the band structure of ytterbium is represented by the scheme shown in Fig. 6, it is possible to account for the observed electrical behavior.

After a small compression, the 6s and 6p bands no longer overlap, and the valence band is now full, and the 6p is the conduction band. The gap increases, until the 5d intersects the 6p band, at which time the 5d becomes the conduction band. The gap increases as long as the conduction band is 6p, and decreases when the 5d becomes the conduction band. When the 5d band

intersects the 6s band, the metallic properties would reappear.

An apparent problem with the simple picture that has been presented is the fact that the resistivity continues to rise after the gap begins to decrease. This can be accounted for in the following manner. The multiplicity in the d-band is higher than in the p-band. Consequently, the effective mass of the electron will be higher than in the p-band. Because the effective mass appears to a high power in the mobility of the electron, it is not unreasonable that the resistivity increases even though the gap has become smaller.

When the techniques have been further developed than they are at the present time, it should become possible to test whether the simple picture that has been presented to explain the semiconduction is correct, or at least compatable with all of the known facts.

This picture of ytterbium in no way negates Hall's proposal of the electronic transition to account for the crystallographic transition. All of the semiconducting phenomena occurs in the α phase. The β phase is a normal metal, even when the pressure is reduced below the transition point.

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Figure Captions

Figure 1. Resistance-pressure curve for ytterbium at 20° C.

Figure 2. Resistance-pressure curves for ytterbium at several temperatures.

Figure 3. Resistance-temperature determinations for ytterbium at several pressures. Circles refer to heating runs and triangles to cooling runs.

Figure 4. Temperature-pressure phase diagram for ytterbium showing the phase line of the α-β transition.

Figure 5. Energy gap of ytterbium as a function of pressure.

Figure 6. Postualted bandstructure of ytterbium. The energy gap causing the semiconducting behavior is the triangle bounded by the 6s, 6p, and 5d bands.

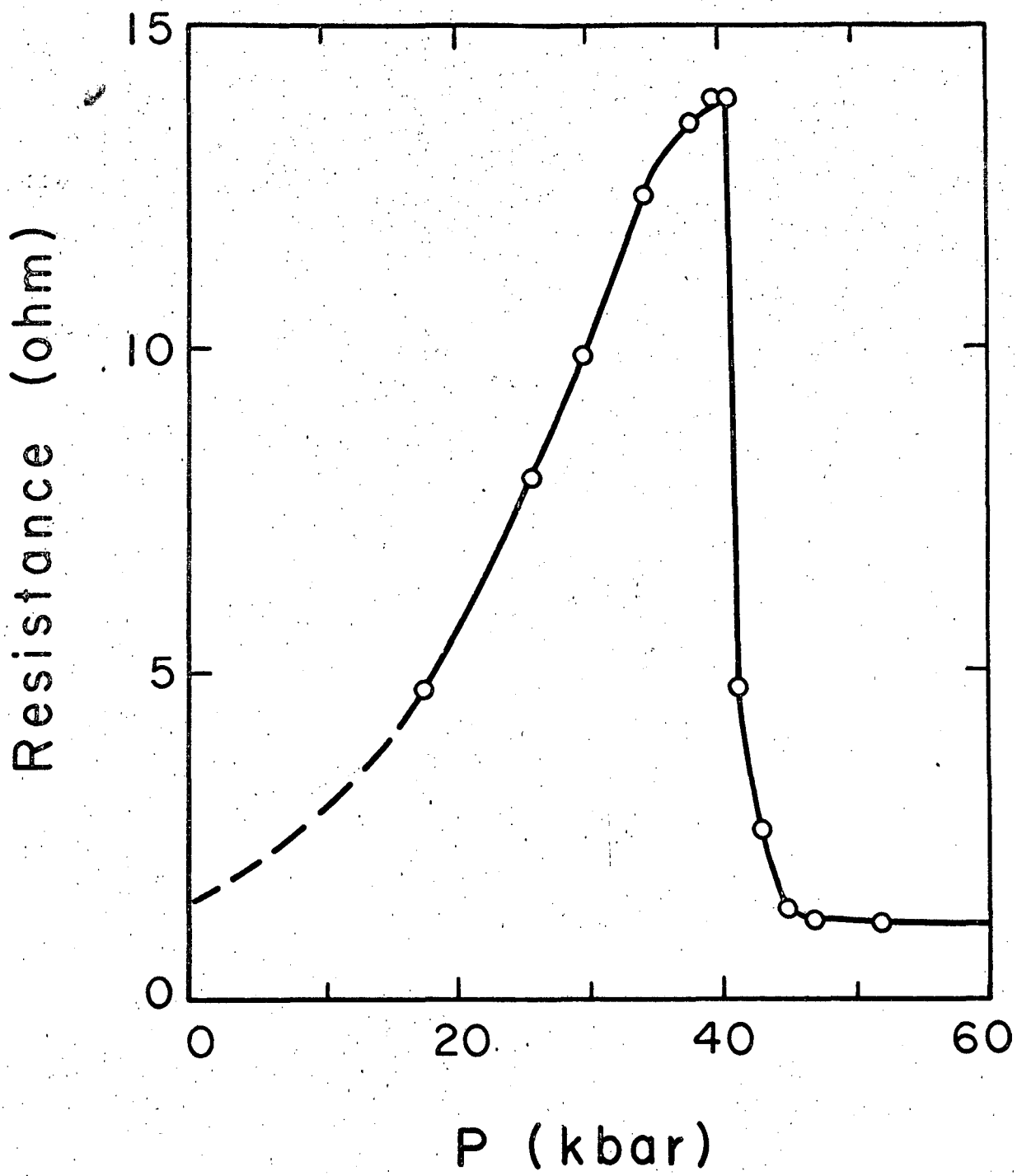

Fig. 1.

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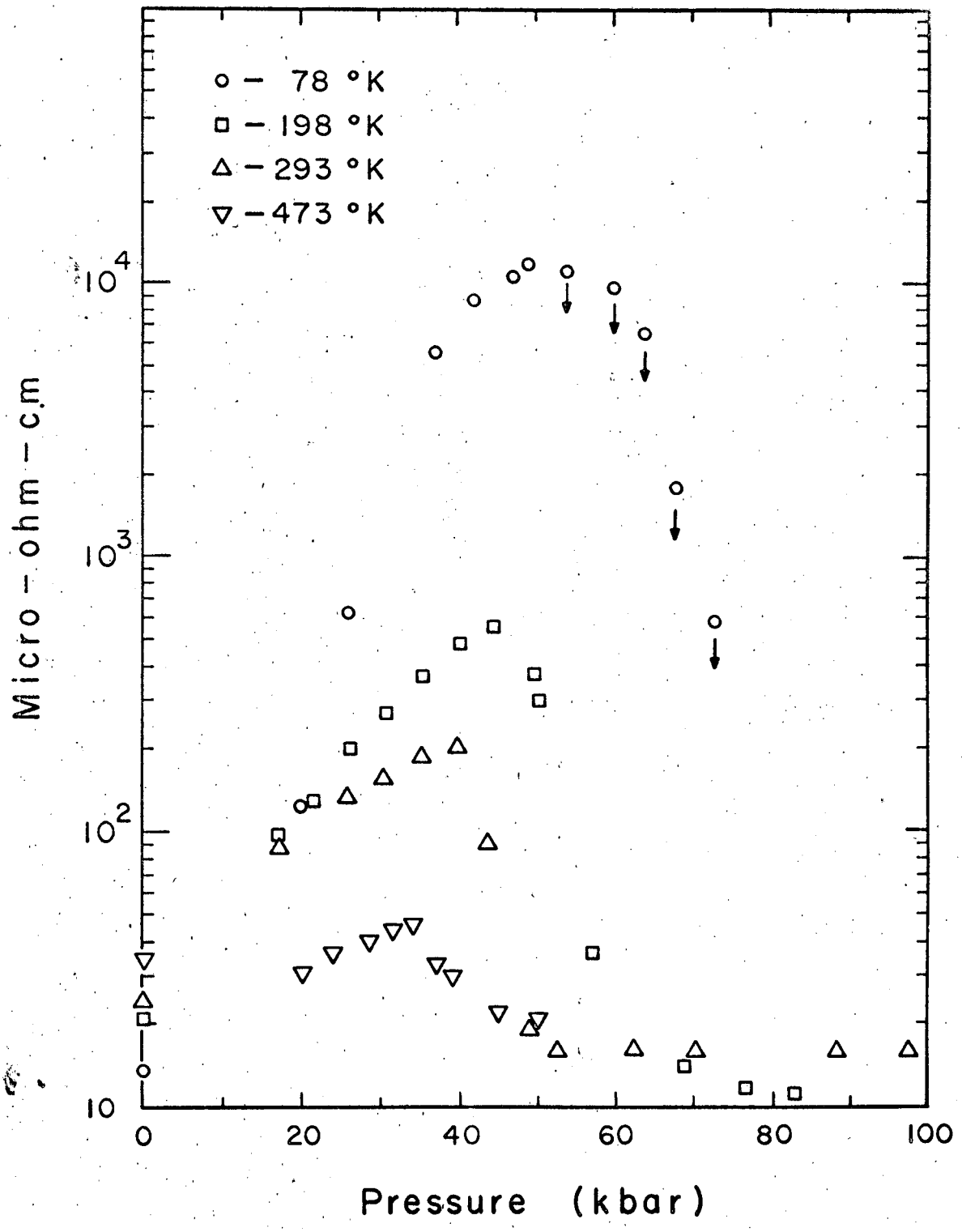

Fig. 2.

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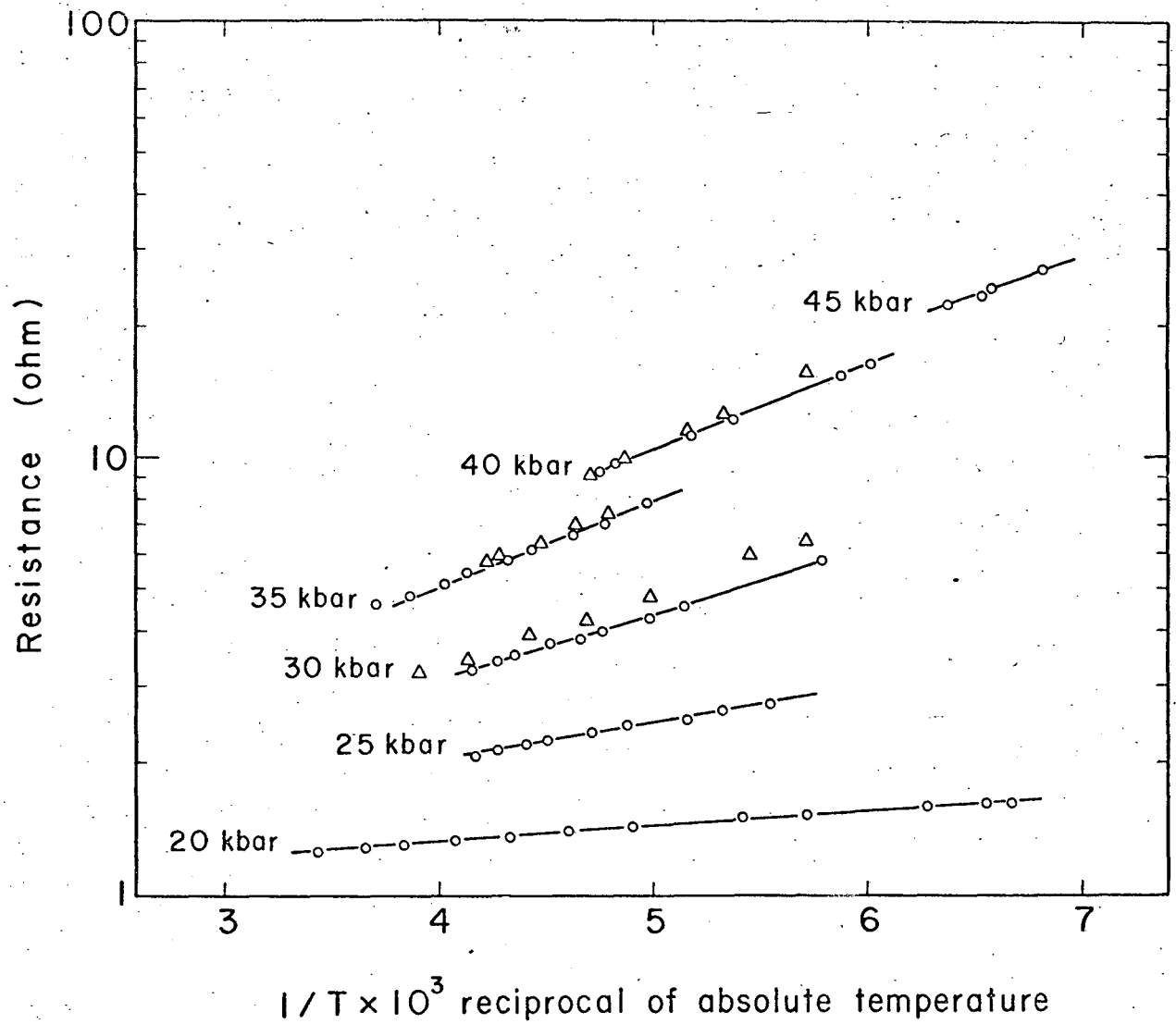

Fig. 3.

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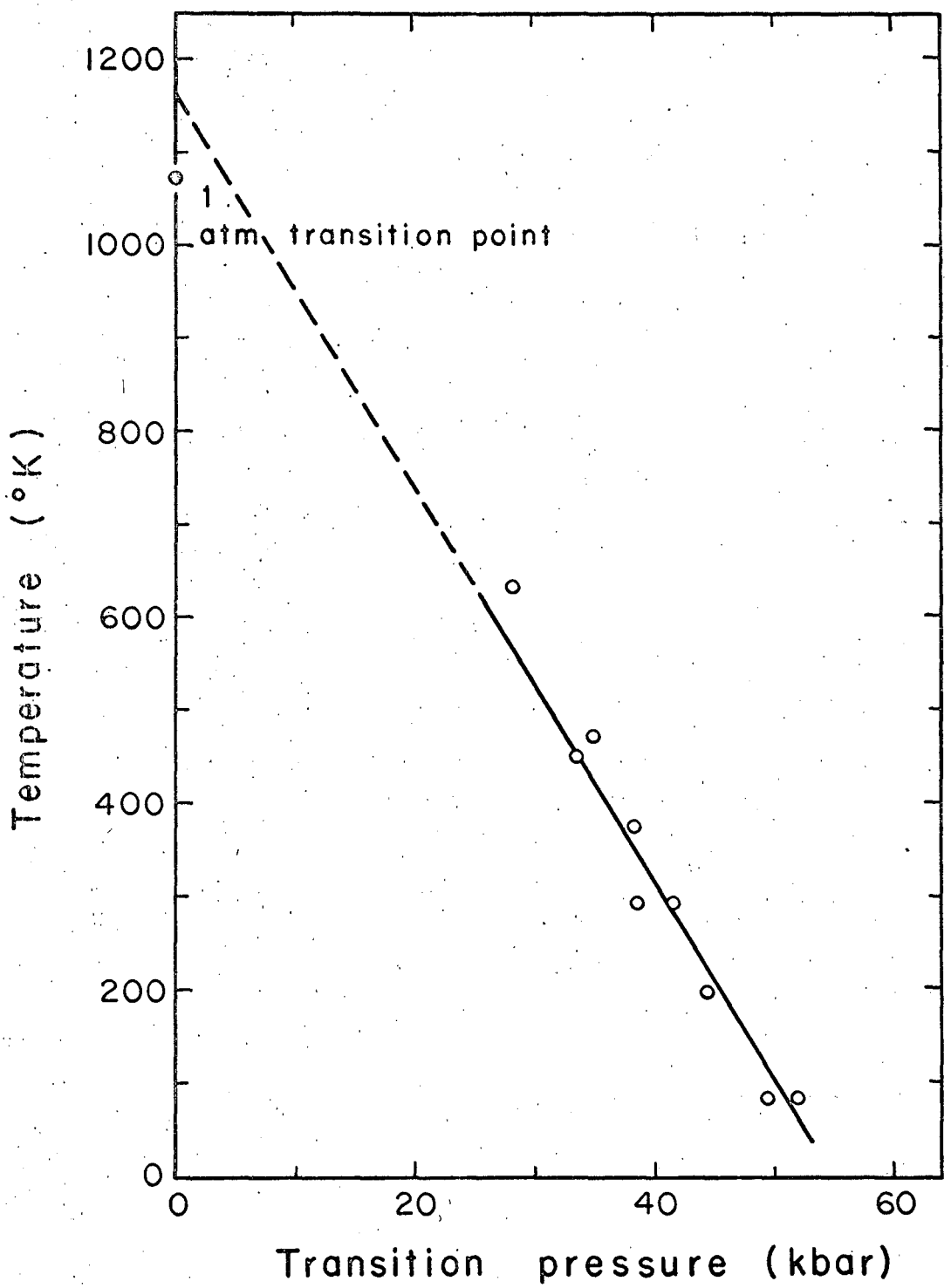

Fig. 4.

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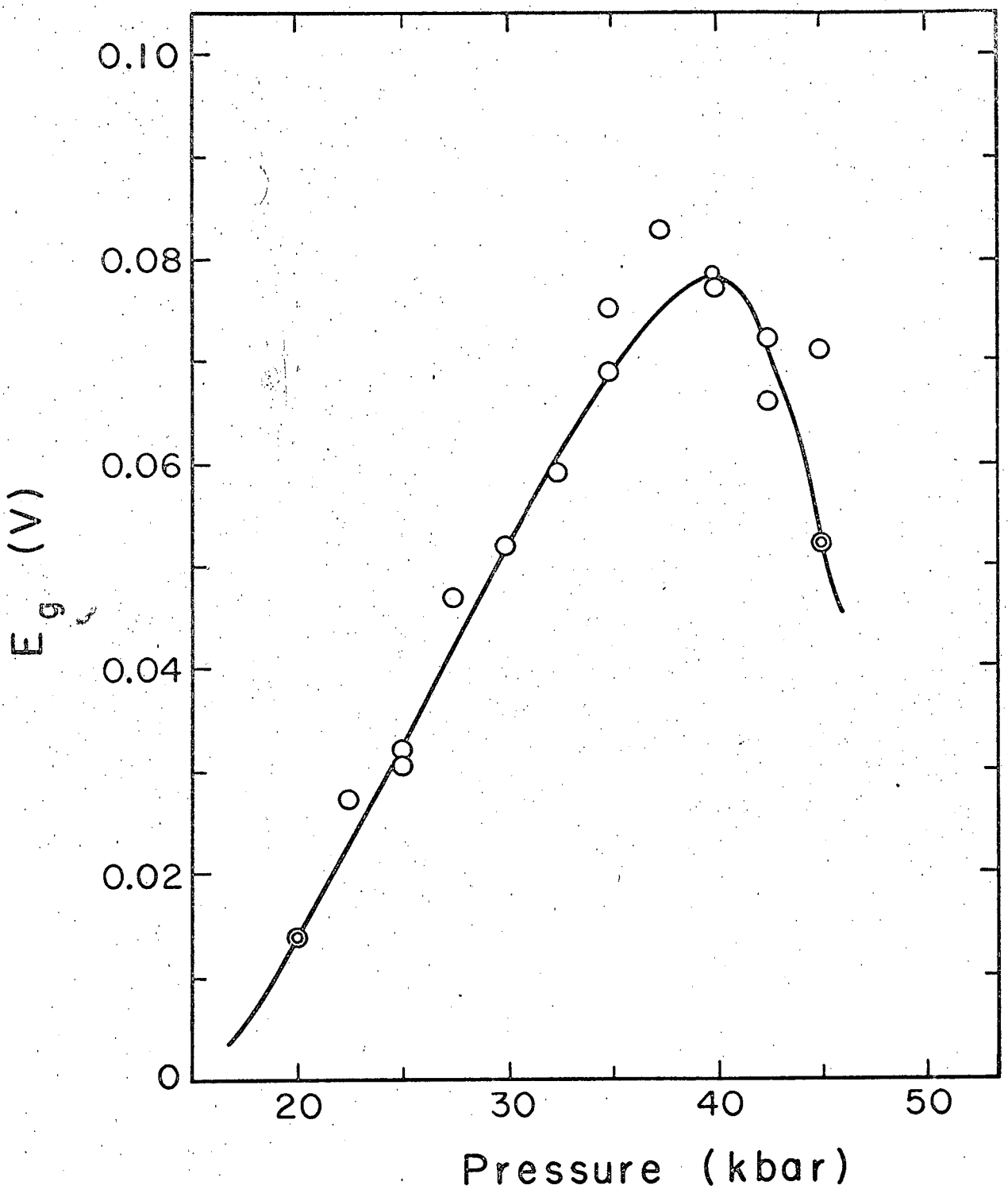

Fig. 5.

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