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20 March 1963

Semiconducting Region of Ytterbium

Abstract. *The resistivity of elemental ytterbium at room temperature rises, by a factor of 11, to a maximum at a pressure of 40 kilobars; a further increase in pressure causes a polymorphic transition; the new phase has a resistivity 80 percent of that of the metal at 1 atmosphere. In the temperature-pressure diagram, the phase boundary has a negative slope. The phase boundary, determined from −190° to 360°C, is a straight line that may be extrapolated nearly to the known α-β transition at 1 atmosphere. Between the transition pressure and 20 kbar, the lowest pressure at which the measurements were made, ytterbium behaved as a semiconductor. The temperature coefficient of resistance is negative; at constant pressure, the resistivity shows the exponential temperature dependence characteristic of a semiconductor. The parameter in the expontial would correspond to an energy gap 0.015 ev at 20 kbar, an increase with pressure to a maximum of 0.080 ev at 37 kbar, and then a decrease to 0.05 ev at 45 kbar.*

In 1954 Bridgman (*1*) published the pressure-volume relationships (to 39 kbar) and the resistivity (to a presumptive 98 kbar) 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 was incorrect. In the following discussion, his figures are corrected where possible to conform to a pressure scale based on the bismuth 1–2 and 6–8 transitions occurring at 25.5 and 88 kbar, respectively.

Particularly intriguing were the results on ytterbium. Bridgman found that at room temperature the resistance of ytterbium increased 11-fold at a pressure of 40 kbar and then rapidly decreased to a value which was 79 percent of that at 1 atmosphere. This value remained nearly constant to about 80 kbar. Vereshchagin *et al.* (*2*) obtained similar results and found that the resistance beyond the peak remained level at least to 200 kbar. Our own work indicates a shallow minimum at about 80 kbar. Both Bridgman and Vereshchagin suggested that the resistance peak represented a polymorphic transition. Recently Hall and co-workers (*3*) verified that a phase change occurs and that the crystal structure changes from face-centered cubic to body-centered cubic. Such a change is known to occur at 1 atmosphere at 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 kbar. From 1 atmosphere through 6 kbar, the temperature coefficient of resistance was normal for a metal in that the resistance increased with the temperature. At 7 kbar there was a decrease in resistance as the temperature increased from 0° to 100°C, and then the resistance started to increase in the manner characteristic of a metal. Bridgman suggested that ytterbium was being squeezed into a semiconducting state. It is this behavior that is the prime subject of our 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 kbar. In the region between 20 kbar 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.

The ytterbium (*4*) was supposedly 99.9 percent pure. Spectral analysis (*5*) showed the following percentages of impurities: Al, 0.015; Ca, 0.03; Fe, 0.025; and Mg, 0.01; if other elements

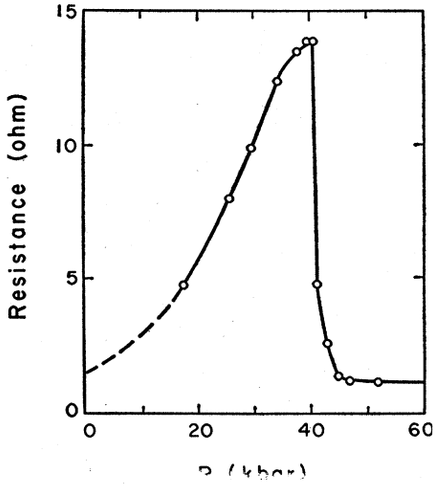

Fig. 1. Resistance-pressure curve for ytterbium at 20°C.

were present the quantities were not detectable by ordinary spectrographic analytical techniques.

The metal was extruded into wire 0.003 inch in diameter; it was then annealed in an argon atmosphere for 15 minutes at 400°C. The Bridgman anvils, silver chloride disks, and pressure measurements have been described (*6*). 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 source. The resistance of the anvils in direct contact was on the order of 30 μohm. 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 neg-

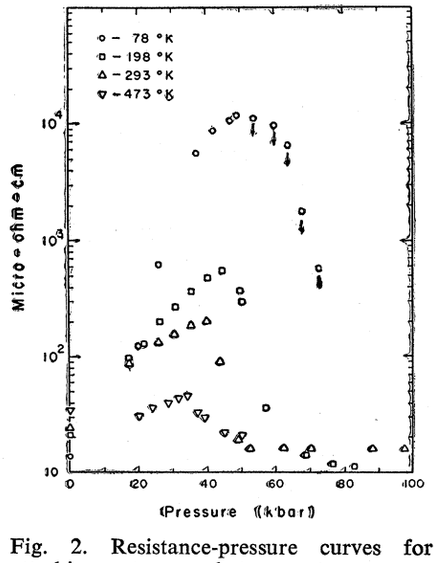

Fig. 2. Resistance-pressure curves for ytterbium at several temperatures.

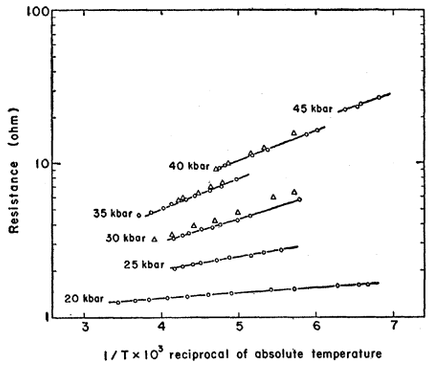

Fig. 3. Resistance-temperature determinations for ytterbium at several pressures. Circles refer to heating runs and triangles to cooling runs.

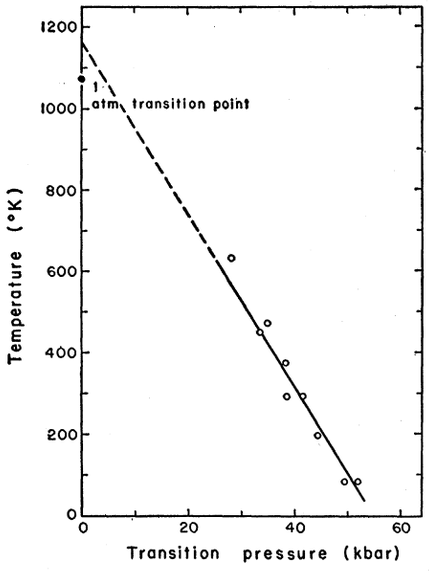

Fig. 4. Temperature-pressure phase diagram for ytterbium showing the phase line of the α-β transition.

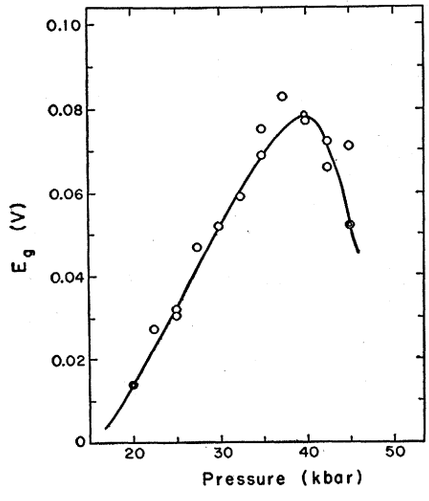

Fig. 5. Energy gap of ytterbium as a function of pressure.

ligible 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 in opposite directions. The isothermal determinations at dry-ice and liquid-nitrogen temperatures were made by immersing the assembly in baths of dry ice and isopropyl alcohol or liquid nitrogen. For the measurements at constant pressure, the system was immersed in a bath of Kanolt No. 40 solution (*7*); it was quite fluid even at 140°K.

Temperatures were determined with two copper-constantan 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 voltage readings were the averages of the results obtained with the current 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.

Figure 1 shows an isothermal determination of the resistance of ytterbium as a function of pressure at 20°C. There is a sharp break in the resistance at 40 kbar, the α-β transition. To obtain this sharp drop, it is necessary to wait about 2 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 entirely 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 may be

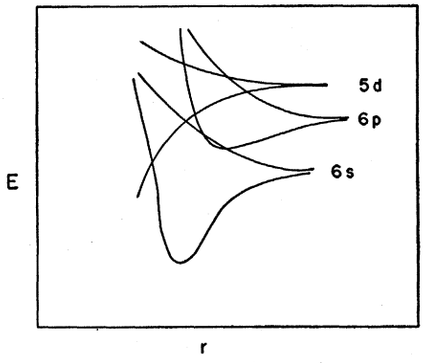

Fig. 6. Postulated band structure of ytterbium. The energy gap causing the semiconducting behavior is the triangle bounded by the 6*s*, 6*p*, and 5*d* bands.

extrapolated nearly to the observed transition pressure at 1 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 shows some of the measured isotherms from 77°K to 600°K. The points at 1 atmosphere are those of Spedding (*8*). 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 the logarithm of the resistance (log R) is plotted against the reciprocal of the absolute temperature ($1/T$). 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 was reached 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 by pieces or bits at these low temperatures. It has been observed by us that frequently the bismuth 1–2 transition at −80°C occurs in steps. Sometimes 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 shown in Fig. 3. The maximum observed resistivity 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 (Eg) 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 percent, it is evident that this gap is not the intrinsic value but rather attributable to impurities. 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 electron structure of ytterbium. First, let us consider the values of the resistances. 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 (*9*) of the electron between the 4*f* and 5*d* levels could not account for this very large increase.

The electron configuration of ytterbium in the gas phase is $4f^{14}5s^25p^66s^2$. The magnetic susceptibility data of Lock indicate that in the solid only 1/250 of the 4*f* electrons are in the 5*d* 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 agrees with the data on 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 is very close to that of barium. This means that the original conductivity is the result of the overlap of the 6*p* and 6*s* 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 6*s* and 6*p* bands no longer overlap, and the valence band is now full, and the 6*p* is the conduction band. The gap increases, until the 5*d* intersects the 6*p* band, at which time the 5*d* becomes the conduction band. The gap increases as long as the conduction band is 6*p*, and decreases when the 5*d* becomes the conduction band. When the 5*d* band intersects the 6*s* 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.

This picture of ytterbium in no way negates Hall's (*3*) proposal of the electronic transition to account for the crystallographic transition. All of the semiconducting phenomena occur 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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26 March 1963

Homograft Tolerance in Mice: Use of Urethan and Sublethal Irradiation

Abstract. *Adult mice [CBA/J (H-2^k)], which received either a single sublethal dose of x-radiation (500 rad) or urethan plus 500 rad, were given intravenous injections of C3H/HeJ (H-2^k) spleen or bone marrow cells (18 to 42 × 10^6 cells per mouse) or both, for 3 days. C3H/HeJ tail-skin homografts were retained (over 130 days) by these mice, whereas BALB/cJ (H-2^d) homografts all were rejected within 33 days. Similarly irradiated or urethan-treated controls (or controls treated with a combination of both), which did not receive C3H cells, rejected both homografts. Specific homograft tolerance is induced in adult mice by this procedure.*

Induced tolerance to homografts, after parenteral administration of allogenic cells into newborn mice, is well-established (*1*), but similar attempts to produce this tolerance in mature recipients, fully competent immunologically, have proved more difficult.

To produce tolerance across the H-2 histocompatibility barrier in adult mice, the recipients must be subjected to lethal whole-body x-irradiation and then to infusion of allogenic bone marrow cells. Long-term survivors from this treatment are tolerant of skin homografts (*2–4*) and contain donor cells specifically tolerant of the host (*2*). In both these situations, specific unresponsiveness to skin homografts is associated with cellular chimerism. Homograft tolerance in nonirradiated adult recipients has been achieved, but only with mouse strains differing unilaterally at the H-2 locus—for example, parental strain recipients (C3H) and (A × C3H)F_1 hybrid cell donors (*5, 6*). This was accomplished by repeated intravenous injections of numerous viable F_1 hybrid spleen cells (up to 1.5 × 10^9 cells) into the parental strain recipients. Cells similarly injected in the strain combinations (C57B1 × C3H)F_1 hybrid----→ C3H and A----→ C3H failed to produce skin homograft tolerance (*6*).

Very recently, Michie and Woodruff (*7*) reported specific homograft tolerance in sublethally x-irradiated (500 r) parental strain mice (A-strain) which received multiple massive intravenous and intraperitoneal injections of (CBA × A)F_1 hybrid spleen cells. To study the induction of specific tolerance to