Metal-Semiconductor Transition in Ytterbium and Strontium at High Pressure

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It has been suggested that Yb and Sr undergo semimetal-to-semiconductor transitions under pressure. We have measured the electrical resistivity ρ from 298 to 2°K at different pressures up to 50 kbar. In Yb, ρ at 4.2°K increases by a factor of 6×10^4 at $P=25$ kbar and saturates at higher pressures. For $P<25$ kbar, we find the empirical relation at 4.2°K $\ln[\rho(P)/\rho(1\text{ atm})]=0.45\ P$, where P is the pressure in kbar. At $P=25$ kbar, the resistance ratio $\rho(4.2°\text{K})/\rho(298°\text{K})=220$. In Sr the resistance rise is much less dramatic, ρ at 4.2°K increasing by a factor of 50 in 35 kbar. A small negative temperature coefficient of resistivity appears for $P\gtrsim30$ kbar in Sr. We suggest that Yb becomes a semiconductor at high pressures, whereas Sr remains a semimetal. These conclusions are compatible with the band-structure calculations of Vasvari, Animalu, and Heine for the fcc alkaline-earth metals, if the effects of spin-orbit coupling are included. We find no evidence for either an excitonic phase or a first-order transition in the neighborhood of the semimetal-to-semiconductor transition at low temperatures. However, no definitive statements can be made because of impurity effects. The Yb sample was 99.99% pure according to emission-spectrographic analysis. At higher pressures both Yb and Sr showed the transition to the bcc phase, and in this phase both materials behaved as a good metal and showed no evidence of a magnetic transition.

YTTERBIUM and strontium are divalent, fcc metals which may exhibit a metal-to-semiconductor transition with increasing pressure. The nature of such a transition has been the object of considerable theoretical work in recent years, and Mott[1] has suggested that the transition is not continuous in the limit of zero temperature. More detailed calculations predict the existence of an intermediate excitonic phase at low temperatures which results in a lattice distortion or in the formation of a spin density wave (see Refs. 2 and 3 and references therein). The additional periodicity produced in the lattice will introduce energy gaps into the band structure. Thus one would expect to see a kink in the resistivity as a function of temperature or pressure at the transition to the excitonic phase. Jérome *et al.*[2] and Halperin and Rice[3] suggest Yb and Sr as the most favorable candidates for the excitonic phase. This paper is exploratory in nature and reports measurements of the electrical resistivity of Yb and Sr from 2 to 298°K at different pressures up to 50 kbar. A search was made at low temperatures for an excitonic phase but the results were negative. The data suggest that pure Yb becomes an intrinsic semiconductor with increasing pressure and that pure Sr remains a semimetal. A definitive statement on the existence of the excitonic phase cannot be made because the critical temperature is expected to be a strong function of sample purity. Attempts to purify Yb and Sr were made, but even the best Yb samples were not intrinsic in the semiconducting region.

At room temperature the electrical resistivity of Yb and Sr rises with increasing pressure and then drops sharply.[4] Transitions are observed in compression measurements at 35 kbar in Sr and 40 kbar in Yb, and x-ray diffraction measurements show that the transition is from a fcc to a bcc structure.[5,6] Bridgman[4] found that near room temperature the temperature coefficient of resistivity (R') of Yb became much smaller with increasing pressure and that the coefficient for Sr became slightly negative near 30 kbar. More extensive measurements of the resistivity of Yb from 77 to 473°K by Souers and Jura[7] show that above 14 kbar R' is negative. A linear variation of $\log R$ versus $1/T$ was found over a small temperature range, and the calculated energy gap increased to a maximum of 0.08 eV at 40 kbar. The resistivity in the bcc phase has no further anomalous changes up to 300 kbar.[8] In Sr the negative temperature coefficient has been observed near room temperature only in the region just before the fcc-bcc transition.[4,9] Again metallic properties are observed in the bcc phase up to 500 kbar.[10] The phase diagrams of Yb and Sr have been studied by several authors and are strikingly similar.[7,9,11,12] In both, the bcc phase is stable at high temperature at 1 atm, and the fcc-bcc phase boundary drops in temperature with increasing pressure. An intermediate hcp phase has been reported for both Sr and Yb but has been attributed to the stabilizing effect of gaseous impurities.[13,14] From the published data we arrive at fcc-bcc transition pressures of 40 kbar at 298°K and 51 kbar at 77°K for Yb and 35 kbar at 298°K and

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[5] H. T. Hall, J. D. Barnett, and L. Merrill, Science **139**, 111 (1963).
[6] D. B. McWhan and A. Jayaraman, Appl. Phys. Letters **3**, 129 (1963).
[7] P. C. Souers and G. Jura, Science **140**, 481 (1963).
[8] R. A. Stager and H. G. Drickamer, Science **139**, 1284 (1963).
[9] A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, Phys. Rev. **132**, 1620 (1963).
[10] R. A. Stager and H. G. Drickamer, Phys. Rev. **131**, 2524 (1963).
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[13] D. T. Peterson and R. D. Colburn, J. Phys. Chem. **70**, 468 (1966).
[14] F. H. Spedding, J. J. Hanak, and A. H. Daane, J. Less-Common Metals **3**, 110 (1961).

TABLE I. Characterization of Yb and Sr samples (emission-spectrographic analysis in wt%).

Impurity \ Sample	Ytterbium 1	2	3	Strontium 4	5	6	7
Na	0.00X	...	...	0.00X	0.00X^-	0.000X	0.00X
K	0.000X	...	...	0.000X	0.000X^-	...	...
Mg	0.000X	0.000X	0.00X	0.0X	0.00X^-	0.00X^-	0.0X
Ca	0.00X	0.000X^-	0.X	0.X	0.X	0.X	0.X
Ba	...	...	...	$<X$	0.0X	0.X	0.X
Mn	...	...	...	0.000X	0.000X^-	0.000X^-	0.00X^-
Fe	0.000X	...	$-$0.00X	0.000X	0.000X	0.000X^-	0.00X^-
Cu	0.00X^-	0.000X^+	0.000X	0.000X	0.000X	0.000X^-	0.000X
Al	...	0.000X^-	0.000X	0.00X	0.00X	0.00X	0.00X
Si	0.000X	0.000X	0.000X	0.00X^-	0.00X^-	0.000X	0.00X
Sn	...	...	...	...	...	0.000X^-	0.000X
Pb	...	...	...	0.00X^-	0.00X^-	0.000X	0.000X
Ag							0.000X
At.%							
Mg, Ca, Ba	0.03	0.004	2.2	1.9	1.2	1.4	
Other	0.03	0.007	0.02	0.04	0.05	0.03	
Purity	99.9	99.99	97.8	98.1	98.8	98.6	
$R_{298}/R_{4.2}$	14	50	7	5	4	24	

46 kbar at 77°K for Sr. Since the transitions are sluggish, the actual transition pressure is difficult to determine accurately.

SAMPLE PREPARATION

Samples[15,16] were made from metal purified by fractional distillation.[17] The Sr was purified in three stages. A light fraction of 15% of the charge was driven to the top of the column by heating the column to 500°C and the collector to 518°C. A high-purity fraction consisting of 35% of the charge was collected by reducing the collector temperature to 350°C for sample 5 (Table I) and 370°C for sample 6 with a source temperature of 525°C. The remainder of the charge was left behind in the crucible and baffle plates. The collecting conditions, with a source temperature of 525°C, were 2.4 cm^3/day.[18] Ytterbium purification was carried out under similar conditions. High-vapor-pressure contaminants, however, were collected on the temperature-controlled finger and the high-purity fraction on the upper baffle plates. The conditions were the following: source temperature 540°C, upper baffle temperature 450°C and cold-finger temperature 80°C. The resulting collection rate was 1.4 cm^3/day.[19]

The samples were analyzed by emission spectrographic analysis and their resistivity ratios were determined either by eddy-current decay or by direct dc measurement. The results are shown in Table I. A Yb sample (No. 1) of high purity was kindly provided by Professor F. H. Spedding and Professor B. Beaudy at the Ames Laboratory, Iowa State University. A Sr sample (No. 4) was taken from the stock used in the x-ray and phase-diagram studies.[6,9] These and the starting materials Yb (No. 3) and Sr (No. 7) are also listed in Table I.

It was found that the resistivity ratio ($R_{300}/R_{4.2}$) of Yb decreased by almost a factor of 10 when the samples were plastically deformed. Subsequent vacuum annealing (10^{-9} Torr) at 200°C for 15 h resulted in partial recovery of these specimens. Small rectangular or hoop-shaped samples were cut and shaped using surgical tools. The Yb samples were annealed after shaping and just prior to loading into the high-pressure apparatus.

EXPERIMENTAL

The pressure was generated either in a girdle die (Fig. 1) or in Bridgman anvils. To avoid ductile-to-brittle transitions, the support jackets were made of Discaloy. The samples were made in the form of hoops or rectangular bars and pressure contacts made to gold-plated molybdenum leads. Two samples from different sources were run simultaneously in order to compare them directly. The pressure medium was AgCl. The pressure calibration is relative to the transitions observed in the electrical resistance of an axially mounted Bi wire and assumes a linear relation between applied load and pressure with fixed points at the origin, 25.4 kbar (Bi I-II) and 80 kbar (Bi III-IV). The fcc-bcc transition in Yb and Sr at 298 and 77°K were also used as calibration points. In the Bridgman-anvil geometry two straight wires were mounted in the cell and Mo leads brought out through Isomica gaskets.[20]

The high-pressure die was put in a cryostat capable of delivering a 100–200 ton load to a chamber at liquid-helium temperature.[20] The temperature was measured by three chromel-versus-Au 0.02 at.% Fe thermo-

[15] Yb purchased from Research Chemicals, Division of Nuclear Corp. of America, Phoenix, Ariz.
[16] Sr purchased from United Mineral and Chemical Co., New York, N. Y.
[17] P. H. Schmidt, J. Electrochem. Soc. **113**, 201 (1966).
[18] R. E. Honig, RCA Rev. **23**, 567 (1962).
[19] C. E. Habermann and A. H. Daane, J. Chem. Phys. **41**, 2818 (1964).
[20] D. N. Lyon, D. B. McWhan, and A. L. Stevens, Rev. Sci. Instr. **38**, 1234 (1967).

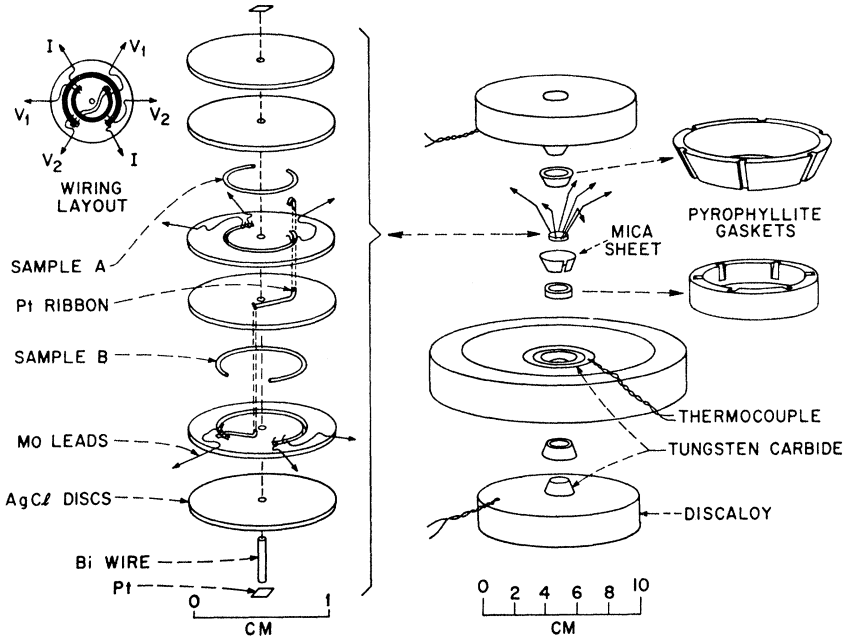

FIG. 1. Girdle die assembly (right) and sample assembly (left).

couples mounted as shown in Fig. 1. The thermocouples were calibrated against the superconducting transition temperature of samples of Tl, Sn, Pb, and Nb mounted in the girdle and also against the boiling temperatures of He, H_2, N_2, and O_2. All measurements were relative to a junction at the ice point. A calibration run was also made with a thermocouple in the cell at 1 atm to determine the temperature gradient across the high-pressure die. In the anvil geometry the average of the temperature measured on each anvil was used. An experiment was performed with a Mo sheet between the Isomica and AgCl disks, and the temperature of the Mo was the same as the average of the anvil temperatures to within ± 0.1°K below 20°K. At present the accuracy of the temperature measurement is about 0.1°K at liquid-helium temperatures and 1°K above liquid-nitrogen temperature. By pumping on the helium bath, temperatures as low as ≈ 2°K can be reached. In order to minimize straining the sample, the pressure was increased near room temperature and then the apparatus was cooled at constant load. The applied load must be adjusted when pumping on the He bath to keep the load on the die constant. It is assumed that negligible change in pressure occurs when the load applied to the die is kept constant on cooling. In some of the experiments the pressure was increased at 77°K in order to attain higher pressures before going through the fcc-bcc transition.

As shown in Fig. 1, the dc resistance was measured by a four-probe method. The current, sample potentials in both directions, thermocouples, and load cell were all recorded digitally, and the data processed by computer. Smooth curves were then drawn through the computer plots.

In order to compare the results of all the measurements a run was made with Yb (sample 1) and Sr (sample 4) in the same cell. The resistance as a function of pressure was measured at room temperature up to ≈ 50 kbar and converted to an approximate resistivity by normalizing the resistivity at 1 atm and room temperature to 26.4 $\mu\Omega$ cm (Yb) and 21.5 $\mu\Omega$ cm (Sr).[21] All the isobars were then normalized to these curves. This procedure is not entirely justified because of the variability of the true resistivity resulting from strain and purity. However, the errors introduced are much smaller than the pressure effects in which changes of several orders of magnitude were observed. Also the data were not corrected for changes in the area-length ratio of the sample with pressure; assuming hydrostatic compression, this would reduce the calculated resistivity by about 10% at 50 kbar.

RESULTS

The measurements on Yb made in the girdle die are summarized in Figs. 2 and 3. Figure 2 gives the pressure dependence of the resistivity at 4.2 and 298°K. Considering the wide range of purity, the points at high pressure show relatively small differences. A close examination of the 4.2°K points suggests that the purer samples have the larger slopes, but this effect is within the experimental error. In the bcc phase Yb is again a good metal, with a resistivity ratio similar to that at 1 atm. Some of the observed isobars are shown in Fig. 3; the resistivities were calculated using the area-length ratio measured before loading the sample. The top four

[21] G. T. Meaden, *Electrical Resistance of Metals* (Plenum Press, Inc., New York, 1965).

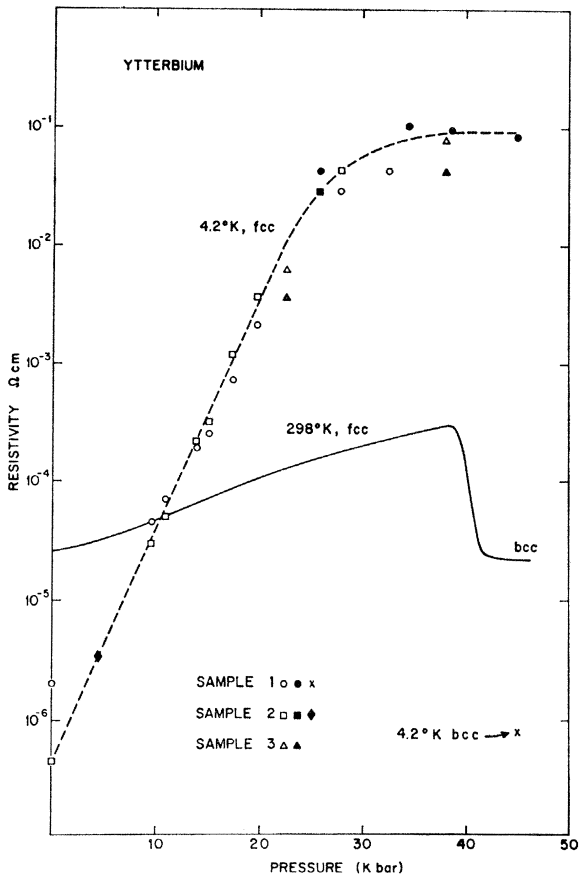

FIG. 2. Resistivity of Yb versus pressure at 4.2 and 298°K. The points for the 4.2°K isotherm are the terminal points of isobars normalized to the 298°K isotherm which was determined in a separate experiment.

curves are from a different run and have been displaced upward by a factor of 10 so as to separate them from the other curves. The curve at 1 atm was obtained in a conventional cryostat. As can be seen in Fig. 3, the temperature coefficient of resistivity becomes negative at about 11 kbar. At the lowest temperatures the resistivity is almost independent of temperature up to $\approx$25 kbar, but a second small rise in resistivity with decreasing temperature is observed above 25 kbar in all three samples. A change in slope also occurs in the 4.2°K isotherm (Fig. 2) at 25 kbar. The resistivity of Yb below liquid-nitrogen temperatures is very dependent on strain. In one run with sample 2, where the hoop had been severely cold-worked before loading, the resistivity in the 20–30-kbar range was down by an order of magnitude, and the resistivity had a pronounced minimum as a function of temperature around 12°K. In another run, a sample was cooled at 5 kbar and the pressure increased at 4.2°K to 23 kbar, where the gasket blew out, thus terminating the experiment. The resistivity rose smoothly and increased by a factor of 1.86×10^3. This is in rough agreement with the cold-worked sample, suggesting that the sample is strained severely when the pressure is increased at low temperatures.

The measurements on Sr are summarized in Figs. 4 and 5. Samples 4 and 5 in Fig. 5 were run in the Bridgman anvil geometry. As noted in Table I, the Sr samples are less pure than the Yb samples, and it is not clear if "pure" Sr will exhibit a negative temperature coefficient at low temperature and high pressure. Samples 4 and 5 show a negative coefficient, whereas sample 6 does not. Sample 6 differs from the other two samples in that it has a substantially higher resistivity ratio at 1 atm and it probably has a much lower gaseous-impurity content because it has been freshly distilled, whereas samples 4 and 5 had been stored under Nujol for several years. Samples 4 and 5 could be more representative of pure Sr than sample 6 because the gaseous and metallic impurities may combine, thus decreasing the number of effective charged impurities. A comparison of Fig. 2 with Fig. 4 and of Fig. 3 with Fig. 5 shows that the behavior of Sr samples 4 and 5 is very similar to that of Yb but that the size of the effects are smaller in Sr than in Yb. With increasing pressure the resistivity of Sr at 4.2°K only rises two orders of magnitude instead of 5 for Yb. The negative temperature coefficient appears somewhere around 30 kbar instead of 10 kbar as in Yb and the largest rise in resistivity with decreasing temperatures is only a factor of 2 for Sr, whereas it is 300 for Yb.

The similarity of the phase diagrams of Yb and Sr suggests that they should form a solid solution and that a smooth variation in the properties should be observed. A few measurements were made on a series of alloys from 77 to 298°K and the results, which are presented in the Appendix, do show a smooth exponential decrease in the magnitude of the negative temperature coefficient of resistivity of Sr_xYb_{1-x} with increasing x at 30 kbar.

DISCUSSION

The experimental results in the preceding section are compatible with the predicted band structures for divalent fcc metals. In the original model put forward by Mott and Jones,[22] a crystal composed of divalent atoms is insulating at large interatomic distances with a filled s band and an empty p band. With decreasing spacing the energy gap between the s and p bands decreases and passes through zero. The crystal becomes metallic when the gap is equal to or less than zero and may become semiconducting at still smaller distances, depending on the variation of the band gaps. Recently, Vasvari, Animalu, and Heine[23] have suggested that d states play a significant role, and these authors have calculated the band structure for Ca which is summarized in Fig. 6. The important difference in this model

[22] N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Oxford University Press, New York, 1936).

[23] B. Vasvari, A. O. E. Animalu, and V. Heine, Phys. Rev. **154**, 535 (1967).

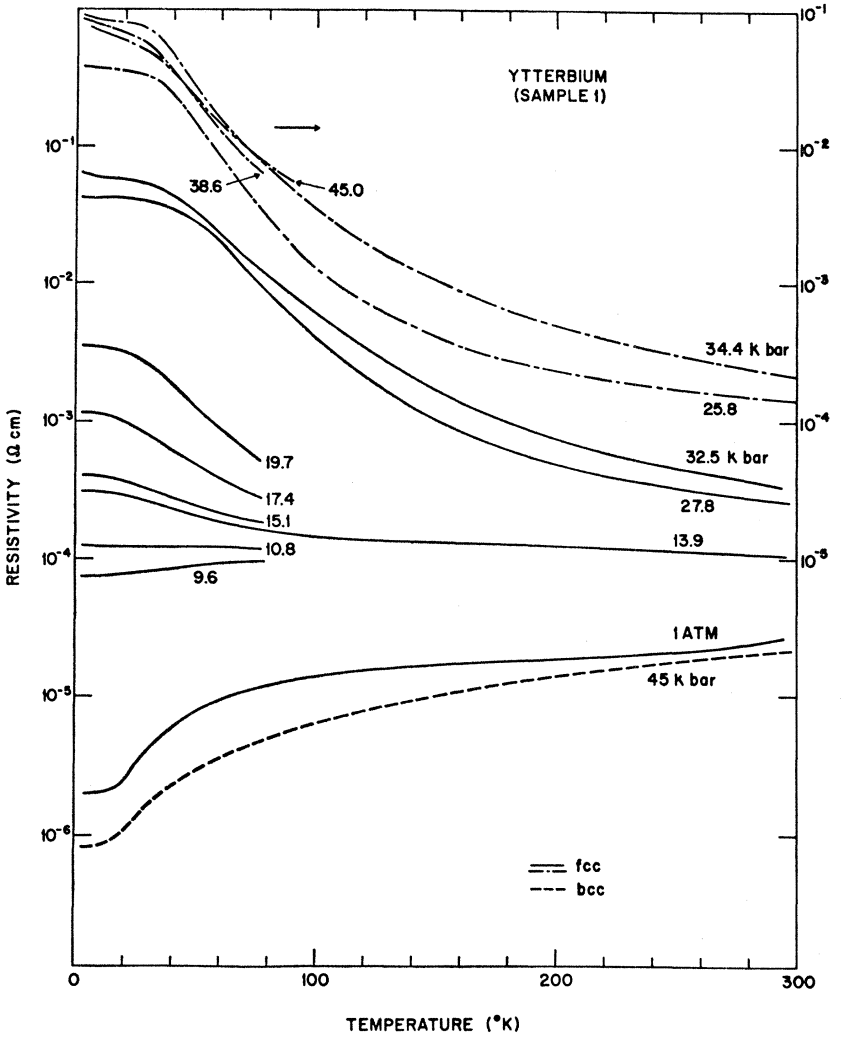

FIG. 3. Resistivity of Yb versus temperature at different pressures. The dashed curves at the top are displaced upward by a factor of 10.

is that a line of degeneracy exists between the first and second bands between W and L. As the volume decreases, the energy difference between W_2' and L_2' becomes smaller and the Fermi surface shrinks. Because of the degeneracy, the Fermi surface cannot shrink to zero but will become a ring of connected "sausages" of alternating pockets of electrons and holes on the hexagonal face of the Brillouin zone. This model predicts that the divalent fcc metals will become semimetals at high pressure but not semiconductors. Spin-orbit coupling will remove the degeneracy and disconnect the sausages.[3] If the spin-orbit energy gaps are larger than the width of each sausage, then the Fermi surface will shrink to zero, and the material will become a semiconductor. The model shown in Fig. 6 is for Ca but the band structure of Sr should be similar to that of Ca at a reduced volume.[23]

The present authors are unaware of any band-structure calculations for Yb in the literature, but the close similarity between so many properties of Sr and Yb would suggest that their band structures are probably not too different, assuming that there is no overlap of the $4f$ bands with the conduction bands in Yb.

The experimental results on Sr and Yb are compatible with the band structure previously described if spin-orbit coupling is included. The residual resistivity rises with decreasing volume, suggesting a decrease in carrier concentration as the Fermi surface shrinks. The resistivity of Sr (sample 6) at low temperature and at pressures $\gtrsim 25$ kbar (the region shown as an insert in Fig. 5) accurately obeys a T^2 law. For $T \lesssim 40$°K, we find $R = R_0 + BT^2$, where $B = 4\times10^{-9}$ and 8×10^{-9} Ω cm°K^{-2} at 34 and 46 kbar, respectively, while at larger temperatures the resistivity saturates. This behavior suggests that Sr is semimetallic in this region with electron-hole scattering dominating the temperature dependence of the resistivity, and that the effective degeneracy temperature is $\sim$100°K. Yb has a similar temperature dependence of the resistivity for pressures around 8 kbar. At higher pressures, the exponential dependence in Yb suggests semiconducting behavior. This

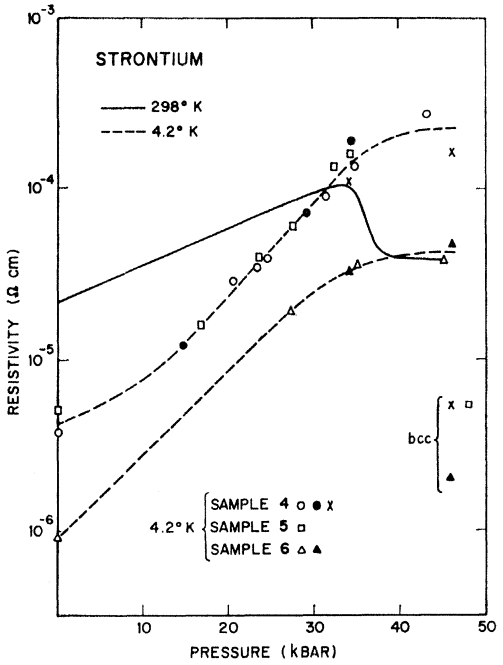

FIG. 4. Resistivity of Sr versus pressure at 4.2 and 298°K. The points for the 4.2°K isotherm are the terminal points of isobars normalized to the 298°K isotherm. Note difference between 4.2 isotherm for samples 4 and 5 and for sample 6.

is in agreement with the model since spin-orbit coupling is undoubtedly much larger in Yb.

Several other models have been proposed to explain the properties of Yb. Rocher[24] suggested that a virtual $4f$ state passed through the Fermi level with increasing pressure and that this resulted in an increase in the resistivity. However, this model will not account for the observed temperature dependence of the resistivity. Coqblin and Blandin[25] have put forward a simplified two-band model with a very narrow $4f$ band laying near the Fermi energy in a free-electron band. This model could lead to the opening up of a semiconducting energy gap with increasing pressure. They then view the subsequent fcc-bcc transition as an electronic transition in which a $4f$ electron is promoted to the conduction band similar to the case of cerium. Hall, Barnett, and Merrill[5] interpreted their x-ray data on the basis of an electronic transition, but the percentage change in the atomic radii of each phase (calculated on a hard-sphere model) is the same for both Yb and Sr and results from the change in coordination number.[6] If the bcc phase had an unfilled $4f$ band, then it might order magnetically. In the present study of the resistivity of bcc Yb down to 2°K, no anomalies were observed which might be associated with spin disorder scattering or other magnetic phenomena. Therefore, at present there is no experimental evidence for an unfilled $4f$ band in bcc Yb. The similarity between Sr and Yb and the agreement with the model of Vasvari *et al.*, if spin-orbit coupling is included, suggest that the $4f$ electrons do not play an important role in fcc Yb. A complete band-structure calculation would be most helpful in this connection.

Recently a phase transition has been found[26] at 1 atm just below room temperature in very pure Yb (commercially available Yb does not show this transition) and the magnetic susceptibility measurements suggest that a small local moment does exist in the fcc phase. As the temperature decreases through the transition

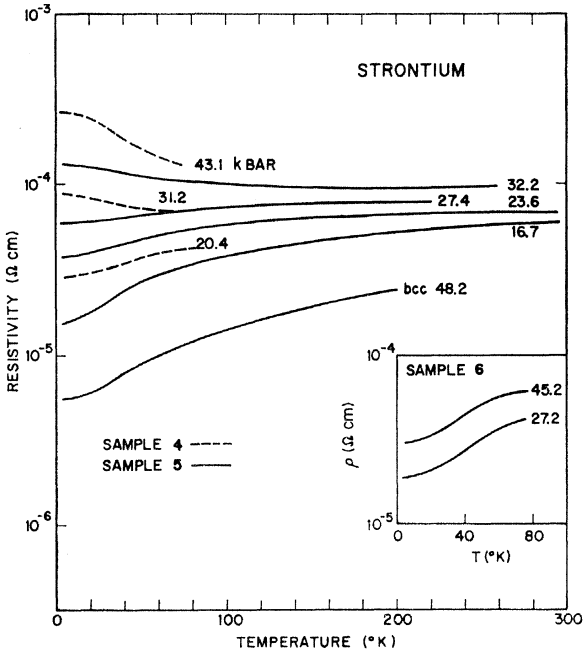

FIG. 5. Resistivity of Sr versus temperature at different pressures. Sample 6 is shown in the inset.

there is a drop in resistivity[26] (on the log scale in Fig. 3 the transition is barely susceptible as a change of slope in the 1-atm curve) and the susceptibility goes from paramagnetic to diamagnetic.[27] The hydrostatic pressure dependence of the transition temperature is -50 to -60°K/kbar,[28] which suggests that our measurements were made on the fcc phase which is stable at room temperature and 1 atm. The susceptibility of the fcc phase follows a Curie-Weiss law at high temperatures, and if the fcc phase is retained at low temperatures by cold-working the sample, a maximum is found around 30°K.[27] This may indicate magnetic ordering. No anomalies in resistivity were found, however, in our experiments which could be attributed to magnetic ordering.

It is difficult to define the critical pressure P_c for the uncrossing of the bands unambiguously from resistivity

[24] Y. A. Rocher, Advan. Phys. **11**, 233 (1962).
[25] B. Coqblin and A. Blandin, Advan. Phys. **17**, 281 (1968).
[26] F. Kayser, Iowa State University (private communication).
[27] E. Bucher (private communication).
[28] A. Jayaraman (private communication).

measurements. We will consider the variation of resistivity with pressure and temperature in a simple two-band model. Balla and Brandt[29] have shown that this model gives value for P_c in Bi in good agreement with the Schubnikov-de Haas effect predictions.[30] However, the results for Yb are ambiguous. In a simple two-band model the resistivity ρ is defined by

$$1/\rho = |e|(n_e\mu_e + n_h\mu_h),$$

where n_e and n_h are the number of carriers in the electron and hole bands and μ_e and μ_h are the respective mobilities.[31] In the absence of galvanomagnetic measurements, it is not possible to separate the pressure dependences of the carrier concentrations and of the mobilities, and we will assume that the mobilities are independent of pressure in the region around P_c. The temperature dependence of the mobility is dominated by lattice scattering and varies as $\mu \propto T^{-3/2}$; however, at low temperatures the mobility is dominated by impurity scattering. In this case the calculated mobility varies as $\mu \propto T^{3/2}$ for charged impurities and μ is constant for neutral impurities. The number of carriers in each band will vary as

$$n_e = n_h \propto \int_{-Eg/2}^{\infty} \frac{E^{1/2}dE}{e^{E/kT}+1}$$

for equal masses. Near P_c on the semiconducting side at high temperatures the mobility is dominated by lattice scattering and the usual result for a semiconductor is obtained in which $\rho(T) = \rho_0 \exp[-E_g/2kT]$. On the semimetal side, as the Fermi energy in each band ($\frac{1}{2}|E_g|$) becomes comparable to kT there will be thermal activation of carriers, and the number of carriers will have increased by a factor of 2 at a temperature $T \approx T_F$, where T_F is the Fermi temperature. At high temperatures the number of carriers will vary as $T^{3/2}$, which will just cancel the temperature dependence of the mobility ($T^{-3/2}$) and result in a resistivity which is independent of temperature. At low temperatures the resistivity will rise and then saturate with decreasing temperature as the number of carriers decreases. This effect will be enhanced if the mobility is dominated by charged impurities. Therefore, the two-band model predicts that the resistivity will vary exponentially with temperature on the semiconducting side and will show a negative temperature coefficient on the semimetal side. The temperature at which the resistivity has dropped by a factor of 2 should decrease as the critical pressure is approached from the semimetal side.

The two-band model also predicts the variation of the residual resistivity with pressure in the semimetal region. The number of carriers will vary as $E_F^{3/2}$, and if we assume that $E_F \propto (1-P/P_c)$, then the residual

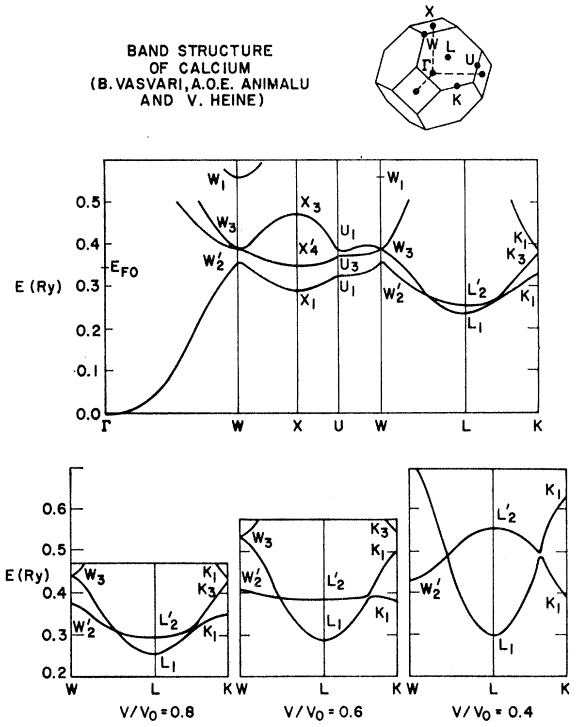

FIG. 6. The calculated band structure of Ca at 1 atm. The bottom three insets show the change in the band structure with decreasing volume.

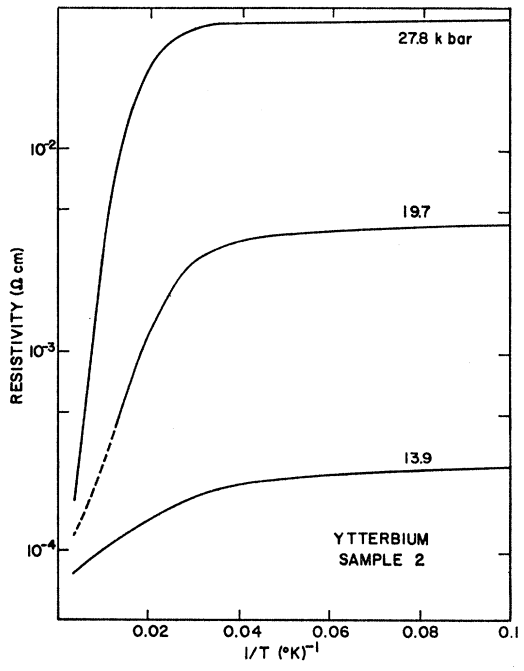

FIG. 7. ρ versus $1/T$ for Yb at different pressures.

[29] D. Balla and N. B. Brandt, Zh. Eksperim. i Teor. Fiz. **47**, 1653 (1964) [English transl.: Soviet Phys.—JETP **20**, 1111 (1965)].
[30] E. L. Itskevich and L. M. Fisher, Zh. Eksperim. i Teor. Fiz. **53**, 98 (1967) [English transl.: Soviet Phys.—JETP **26**, 66 (1968)].
[31] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956).

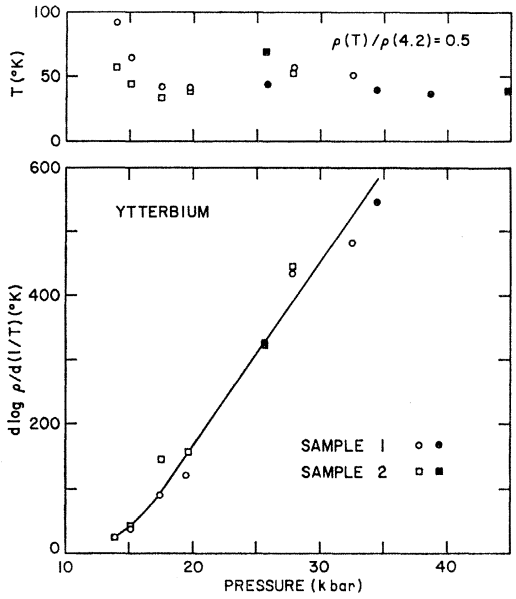

FIG. 8. The slope $d\log\rho/d(1/T)$ versus pressure for Yb (bottom). The temperature at which the resistivity drops by a factor of 2 from the resistivity at 4.2°K versus pressure (top).

resistivity will vary as $\rho_0^{-1}=\sigma_0\propto(1-P/P_c)^{3/2}$ as P_c is approached from the semimetal side.[29] On the semiconducting side the number of carriers resulting from impurities is constant, and the pressure dependence of the residual resistivity would result from small changes in mobility. This should lead to a change of slope in the residual resistivity-versus-pressure curve near P_c.

We can compare the results of the two-band model with the pressure and temperature dependence of the resistivity of Bi which has been measured below P_c. Schubnikov-de Haas measurements show that the area of the electron and hole Fermi surfaces in Bi decreases 60% in 15 kbar, and that the area of the Fermi surface extrapolates to zero at 24–25 kbar.[30] Several authors have found a negative temperature coefficient of resistivity appearing at ≈ 7 kbar and linear log$R$-versus-$1/T$ relations were found over small temperature intervals at higher pressures.[29,32,33] These were interpreted as resulting from semiconducting energy gaps varying from 0 to 0.03 eV. However, Brandt and Balla found that the residual conductivity varied as $(1-P/P_c)^{3/2}$ and they obtained a value of $P_c=24.5$ kbar, which agrees with the Schubnikov-de Haas measurements. The temperature at which the resistivity drops by a factor of 2 decreases with increasing pressure, but the resistivity is not independent of temperature at higher temperatures. In Bi the results are compatible with a two-band model and indicate that an apparent exponential dependence of the resistivity on temperature is not necessarily a good test of semiconducting behavior.

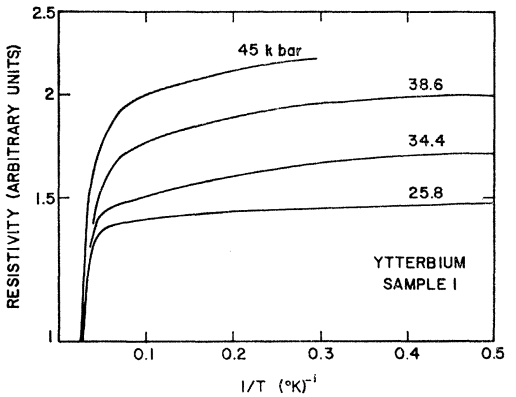

FIG. 9. ρ, on a logarithmic scale, versus $1/T$ for Yb in the low-temperature region. The curves have been displaced vertically from each other for clarity.

The results obtained on Yb are not entirely interpretable on a two-band model. Figure 7 shows three curves of $\log_{10}R$ versus $1/T$ for sample 2, and an exponential temperature dependence is observed over a range 100–300°K at pressures of 19.7 and 27.8 kbar. The measured slopes are summarized in Fig. 8. These results are in reasonable agreement with the earlier measurements of Souers and Jura[7] and suggest that $P_c=14$ kbar and that $dE_g/dP=0.0049$ eV/kbar. However, there is no change in slope at 14 kbar of the curve of the resistivity versus pressure at 4.2°K (Fig. 2), and if P_c is taken as 14 kbar then what is the cause of the change in slope at ≈ 27 kbar? At pressures below 14 kbar a negative temperature coefficient of resistivity is observed down to ≈ 10 kbar and the resistivity is almost independent of temperature at higher temperatures, as predicted by the model (Fig. 3). However, the temperature at which the resistivity drops by a factor of 2 is constant and does not decrease with increasing pressure as shown in Fig. 8. Secondly, the residual resistivity does not vary as $(1-P/P_c)^{-3/2}$. On the contrary, the logarithm of the resistivity at 4.2°K increases linearly with P over a change in ρ of 10^5. Comparison of the observed resistivity with the two-band model only partially supports a value of $P_c=14$ kbar for Yb and a definitive determination will have to await further measurements.

The temperature dependence of the resistivity down to 2°K in the pressure range 10–20 kbar shows no abrupt change in slope, which might reflect the formation of the excitonic phase. A small second rise with decreasing temperature is observed at pressures above 25 kbar (see Fig. 3). One possible explanation of this rise is impurity carrier freeze-out, and from the slope of log-versus-$1/T$ curves (shown in Fig. 9), the activation energy is found to be about 0.5°K. The binding energy of an exciton is of the same order of magnitude, and therefore the critical temperature for the formation of the excitonic phase could be well below our experi-

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mental limit of 2°K. This interpretation of the small rise in resistivity at low temperatures is only one of many. The second rise in resistance is probably not associated with a transition to an excitonic state itself, since one would expect to see a sharp change in the resistivity at the transition—as is observed in chromium, in which a similar loss of carriers from the formation of a spin density wave occurs.[34] Because resistivity measurements can seldon be interpreted unambiguously, a more complete discussion of Yb and Sr at high pressure will have to await further measurements. Until substantially purer material is available, a definitive statement on the existence of an excitonic phase above 2°K in Yb and Sr cannot be made.

ACKNOWLEDGMENTS

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APPENDIX

Yb (sample 3) and Sr (sample 7) were arc-melted together in varying proportions (Sr_xYb_{1-x}, $x=0.1$, 0.3, 0.5, 0.7, 0.9). X-ray diffraction studies at 1 atm of $Sr_{0.5}Yb_{0.5}$ showed single-phase fcc material, and x-ray studies at high pressure showed the fcc-bcc transition observed in the end members. Samples of an alloy and Yb were run simultaneously in the Bridgman-anvil geometry. The fcc-bcc transition pressure increases from either end of the series to a maximum value of ≈ 47 kbar at room temperature at the 50-50 composition. The transition becomes considerably more sluggish in the middle, so that the true increase in the transition pressure may be somewhat less. Figure 10 summarizes the results for the temperature dependence of the resistance.

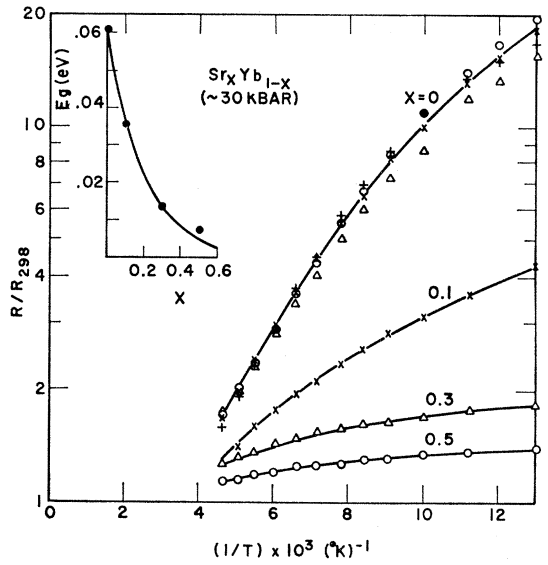

FIG. 10. (R/R_{298}) versus $1/T$ for Sr_xYb_{1-x} alloys. The inset shows the variation in the slope with concentration.

The data are normalized to room temperature. The spread of the points for the pure Yb curve shows the reproducibility of the results. In each run the pressure was increased to the same applied load and a temperature cycle was made. Although this load nominally corresponded to ≈ 30 kbar, some differences in the pressure calibration are to be expected, and the resulting agreement is reasonable. Putting a straight line through the $\log_{10}R$-versus-$1/T$ plots gives slopes as shown in the insert of Fig. 10. The solid curve is given by $E_g=0.061 \times \exp(-5x)$ eV, where x is the mole fraction of Sr. Since the plots of $\log_{10}R$ versus $1/T$ are not linear over any large temperature range, the values of E_g are somewhat arbitrary and the relation is only intended to show that the negative temperature coefficient decreases rapidly but smoothly with increasing Sr content.

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