

are sets of this class of representation which are complete, i. e., the  $\vec{k}\cdot\vec{p}$  representation<sup>15</sup> and the plane-wave representation.

This representation has been used to derive some well-known results. First, expressions for the kinetic momentum and the velocity of the electron in the magnetic field have been derived. Then a generalized Onsager relation<sup>17</sup> for the area in  $\vec{k}$  space was derived. In all cases it was shown that the previous results are to be modified in the same manner, i. e., the wave vector  $\vec{k}$  is to be replaced by the operator  $\vec{k}$  symmetrically. Expressions for the effective mass, the cyclotron mass, and the cyclotron frequency were also derived in a simple

way. Thus the appropriate space for describing the motion of Bloch electrons in the magnetic field is an operator space and not the wave-vector space. The same principle can be applied to the pseudopotential theory of metals in a magnetic field. It has been shown<sup>19</sup> that the vector  $\vec{k}$  in the zero-field pseudopotential is to be replaced by the operator  $\vec{k}$  in the magnetic pseudopotential. Some of the results in the section on dynamics have been derived by Zak<sup>12,13</sup> by using essentially the same representation, though he started out in a different representation, but here they have been rederived in a simple and straightforward way for the sake of completeness.

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## New First-Order Phase Transition in High-Purity Ytterbium Metal

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A first-order magnetic phase transition has been observed in high-purity Yb metal. It is characterized by a paramagnetic-to-diamagnetic transition with a large degree of hysteresis between 100 and 360 °K, and appears to be associated with an fcc-hcp martensitic transformation. The occurrence of this transition is characteristic of high-purity metal and has not been previously reported. Several other properties such as the specific heat at 0 and 106 kOe, the volume and resistance changes the low-temperature resistivity, x-ray data, and the pressure and strain dependence of the transition are discussed. The diamagnetic phase is not superconducting above 0.015 °K. The fcc phase was obtained from the hcp phase by applying strain at room temperature and was also investigated. It shows a strongly temperature-dependent paramagnetic susceptibility down to 1.4 °K, but no magnetic ordering could be detected down to 1.0 °K.

### I. INTRODUCTION

Ytterbium metal is known to exist in three different crystallographic modifications, namely, fcc, bcc, and hcp.<sup>1,2</sup> Of these, the bcc phase is the high-temperature phase while the fcc phase is stable at atmospheric pressure and up to about 660 °C. It

was believed that the hcp phase was impurity stabilized and had a narrow range of stability between about 300 and 700 °C, at atmospheric pressure.<sup>1</sup> High-pressure studies on Yb have shown that the fcc-bcc phase boundary has a negative slope and that a fcc-bcc transition could be induced by pres-

sure at room temperature, by application of 40-kbar pressure.<sup>2-8</sup> The stability region of the hcp phase has been delineated with respect to the fcc and bcc phases and the published phase diagram shows that the hcp phase is unstable below 260 °C and above about 30 kbar.<sup>2</sup>

Unlike the neighboring rare-earth metals, Yb is divalent and because of this exhibits anomalous physical properties in comparison to other rare-earth metals. In fact, it more closely resembles the divalent alkaline-earth metals. Because of the complete filling of the 4*f* shell in Yb, one expects the metal to be nonmagnetic. Lock<sup>9</sup> observed, however, a strongly increasing susceptibility below room temperature and suggested that a small fraction (0.38%) of the Yb atoms might be in the trivalent (<sup>2</sup>F<sub>7/2</sub>) state. Lounasmaa<sup>10</sup> reached a similar conclusion from his low-temperature specific-heat measurements. On the other hand, Gossard *et al.*<sup>11</sup> concluded from the NMR results that Yb metal is nonmagnetic and that Lock's results may be an impurity effect.

Recently, one of us (P. H. S.) succeeded in obtaining Yb metal in a state of very high purity by repeated fractional distillation and condensation. The metal thus condensed exhibited many interesting and hitherto unsuspected characteristics which we have studied in detail. In this paper these results will be presented and discussed.

## II. EXPERIMENTS AND RESULTS

Yb metal as received (Research Chemicals) had a resistance ratio  $R_{298\text{ }^\circ\text{K}}/R_{4.2\text{ }^\circ\text{K}}$  of 9. By repeated distillation at  $10^{-9}$  Torr this ratio was increased to about 100. The absolute purity of the final material was better than 99.95%. Spectroscopic analysis indicated the presence of Ca, Mg, Cu, Si, and Al in the range of few parts per million and gas analysis revealed 430 at. ppm H, while no O and N could be detected.

### A. X-Ray Studies

The x-ray diffraction pattern of the condensed high-purity Yb metal was quite complex and, further, a strong preferential orientation of the crystallites

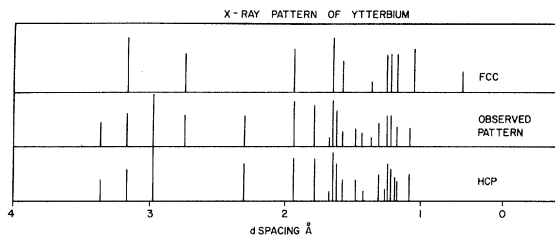


FIG. 1 Debye-Scherrer pattern of fcc and hcp Yb and observed pattern of as-condensed Yb (all taken at room temperature).

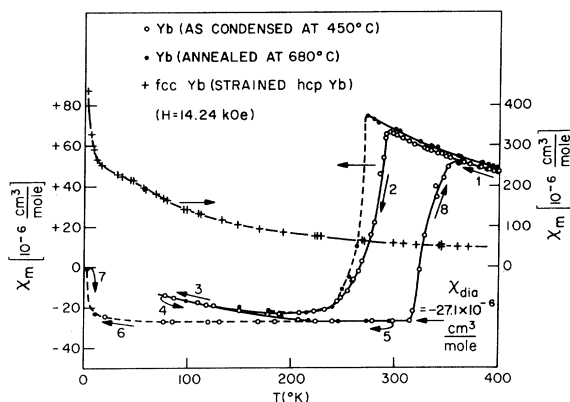


FIG. 2. Susceptibility versus temperature of hcp Yb (as condensed and annealed) and fcc Yb obtained from diamagnetic hcp Yb by plastic deformation.

was evident. However, x-ray powder photographs of filings of the condensed metal exhibited lines characteristic of only the fcc phase, with a lattice constant of  $a = 5.486 \text{ \AA}$ . It was later verified that plastic deformation of the condensed metal removed all the extra lines present in the unstrained material, giving a clean fcc pattern. The relative proportions of these two phases differed somewhat from sample to sample. It was suspected that the structure of the condensed high-purity Yb might be due to some hitherto unnoticed stacking sequence, but our attempts to match the calculated intensities and the  $d$  values of several such sequences with the observed pattern were not fruitful. The complex x-ray pattern could be accounted for if it is assumed that the material consisted of a mixture of fcc and hcp phases. The hcp phase gave  $a = 3.883 \text{ \AA}$ ,  $c = 6.328 \text{ \AA}$  ( $c/a = 1.629$ ) at room temperature. The x-ray powder pattern of the condensed metal and the x-ray patterns of the fcc and hcp phases are shown diagrammatically in Fig. 1, where they are juxtaposed for comparison. The effect of thermal treatment on the structure was also studied. X-ray patterns of the condensed high-purity material recorded at room temperature following annealing at 150 °C showed exclusively lines characteristic of the fcc phase. After dipping such samples in liquid nitrogen, the x-ray pattern at 293° was predominantly hcp with some traces of the fcc phase left.

### B. Magnetic Behavior

One of the most interesting properties of the high-purity Yb is its magnetic behavior. Figure 2 shows the temperature dependence of the magnetic susceptibility of the unstrained Yb. A rather striking magnetic transition from paramagnetic to the diamagnetic state is observed. The transition starts at about 270–290 °K when cooled and on warming the reverse transition begins at about 315 °K. After

some cycling below 300 °K the diamagnetic susceptibility became very reproducible and had a value of  $-27.1 \times 10^{-6}$  cm<sup>3</sup>/mole. It remains constant to about 20 °K and the small rise below 20 °K is probably due to the presence of a few parts per million of Tm or Er impurities or even Yb<sup>3+</sup>. The observed diamagnetic susceptibility is relatively large and comparable to the stronger diamagnetic metals, e. g., Au, Hg, Sn, or Pb. In the same figure are shown the susceptibility measurements taken on a plastically deformed sample of high-purity Yb. It can be seen that the magnetic transition has completely disappeared in the strained material and the sample remains paramagnetic, increasing monotonically with decreasing temperature. At 1.4 °K, the susceptibility shows a marked field dependence in fields up to 15 kOe, indicating that the magnetization originates from localized moments which one begins to saturate (see Fig. 5). This difference in behavior, coupled with the fact that plastic deformation removes the hcp phase indicates that the magnetic transition must be a property associated with the fcc-hcp phase transition. No superconductivity was found in diamagnetic hcp Yb down to 0.015 °K. This is not too surprising since neither the neighboring Lu with also a filled 4*f* shell but much larger electronic specific heat nor the alkaline-earth metals exhibit superconductivity above 0.015 °K at atmospheric pressure.

### C. Resistivity Studies

Resistivity studies on unstrained samples were carried out as a function of temperature down to 160 °K, as shown in Fig. 3. A rather sharp drop in resistivity is observed at the magnetic transition and this anomaly in resistivity exhibits the same kind of thermal hysteresis noticed in the magnetic susceptibility. In the fcc phase, the resistance  $\rho$  was also measured between 1.0 and 30 °K; it was found to vary as  $T^{2.5}$  from 1 to 15 °K and then follow a linear temperature dependence.

The pressure dependence of the magnetic phase

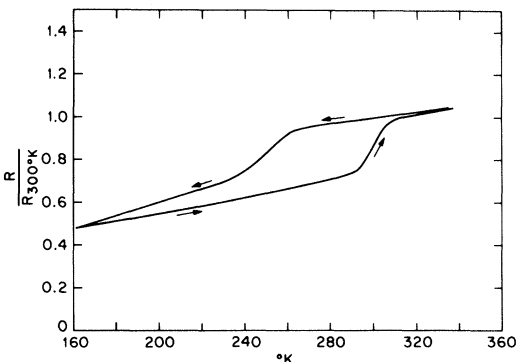


FIG. 3. Resistivity versus temperature of as-condensed hcp Yb for a temperature cycle 340–160–340 °K.

transition was determined by following the resistance anomaly. The pressure dependence is large and the transition temperature is lowered by pressure at a rate of about  $(45 \pm 10)$  °K/kbar. Also, with the lowering of the transition temperature the thermal hysteresis interval broadens.

### D. Thermal Expansion

Thermal-expansion measurements were carried out on a sample of high-purity Yb by the capacitance method of White.<sup>12</sup> At the magnetic phase transition there was a small anomalous thermal expansion, and the relative volume change  $\Delta V/V$  of a sample cooled down to 130 °K and warmed up again to room temperature was found to be  $(2.30 \pm 0.1) \times 10^{-3}$ . Apparently, in going into the diamagnetic state there is a small expansion. This fact is in agreement with the sign of the pressure effect. Combining the  $\Delta V/V$  obtained from thermal expansion and the pressure dependence of the transition temperature, the latent heat  $L$  can be calculated via the Clausius-Clapeyron equation. We find  $L = 25.8$  J/mole at an average transition temperature of 270 °K.

### E. Specific Heat of Yb

Lounasmaa<sup>10</sup> has measured the specific heat of a sample of Yb metal, presumed to be fcc, down to 0.4 °K. Except for a slight upward turn at the lowest temperature the behavior was normal. The electronic specific-heat coefficient had a value  $\gamma = 2.90$  mJ/°K mole and the Debye temperature  $\Theta_D(0) = 118.1$  °K, which suggested an electronic configuration similar to Ba except for a filled 4*f* shell. Our results for the as-condensed high-purity Yb yielded  $\gamma = 3.30$  mJ/°K<sup>2</sup> mole and  $\Theta_D(0) = 117.6$  °K, roughly in agreement with Lounasmaa's<sup>10,13</sup> results. The results on our fcc phase obtained by plastic deformation of the as-condensed high-purity Yb (hcp) are totally different from any value so far measured. We find  $\gamma = 8.36$  mJ/°K<sup>2</sup> mole and  $\Theta_D = 109$  °K. These numbers were found independently in three runs and different samples and do not seem to depend on further deformation, once the sample has been completely cold worked. In Fig. 6,  $C/T$  versus  $T^2$  is plotted for the hcp and fcc Yb. Our large  $\gamma$  value for the fcc phase indicates that Lounasmaa's sample might have been hcp Yb. Our recent susceptibility measurements on his sample, kindly obtained from the Argonne National Laboratory by the permission of Professor Lounasmaa, showed the same type of hysteretic behavior as shown in Fig. 2. Therefore, his data apply to the hcp phase and our results on fcc Yb are entirely new.

For fcc Yb, we also measured the specific heat in a magnetic field of 106 kG. The specific heat differs only very slightly from its zero-field value below  $T = 4.5$  °K but not up to 25 °K and, surprisingly, extrapolates to the same linear term as in zero field.

The purpose of the high-field measurements was to find out whether the large linear term would be field dependent, indicating other than a density-of-states contribution.<sup>14,15</sup>

### III. DISCUSSION

The results presented have clearly established that unstrained high-purity Yb exhibits certain physical properties hitherto unnoticed. The most striking behavior is the magnetic transition accompanying the fcc  $\leftrightarrow$  hcp phase transition. This transition has a finite volume change  $\Delta V$  associated with it and exhibits marked hysteresis. From the clear-cut nature of the magnetic transition and the very reproducible temperature-independent diamagnetism, we believe that the unstrained bulk material is single-phase hcp at low temperatures. The weakly paramagnetic phase, above room temperature or occurring after plastic deformation of the diamagnetic (hcp) phase, must then be identified as the fcc phase, if compared with the x-ray results. There is, however, a noticeable difference between the paramagnetic susceptibilities of an unstrained and strained fcc phase, as demonstrated in Figs. 2 and 4, which cannot be explained at present.

In what follows we will show that all our observations are consistent with the assumption that the magnetic transition consists in a conversion of a small fraction  $f$  (about 0.8%) of  $\text{Yb}^{3+}$  (above the transition) into  $\text{Yb}^{2+}$  (below the transition).

The temperature-dependent part of the susceptibility above room temperature is analyzed using the expression

$$\chi = \chi_0 + fN^2 g_J^2 \mu_B^2 J(J+1)/3R(T - \theta). \quad (1)$$

$\chi_0$  was obtained by plotting  $\chi$  versus  $1/T$  and extrapolating to  $T \rightarrow \infty$ . Otherwise, all the symbols in (1) have their usual meaning. If  $\chi_0$  is assumed to be temperature independent,  $\theta$  and  $f$  are then found by plotting  $1/(\chi - \chi_0)$  versus temperature as shown in Fig. 4. The values of  $\chi_0$  and  $f$  are given in Fig. 4.  $\theta$  cannot be determined accurately but must be small, suggesting that crystal field and exchange effects are small above room temperature. In Figs. 2 and 4 we have plotted the data for two different samples which behave slightly differently in the paramagnetic region. The slight increase in susceptibility after annealing of a sample which had been stored at room temperature for two years is in agreement with the x-ray results. Both x-ray results and susceptibility indicate that the conversion of fcc to hcp is very sluggish at room temperature (295–300°K) but sets in abruptly at 270–290°K when cooling and vice versa when warming at 315–320°K, being complete at around 360–400°K. When cooling, the phase transformation in our highest-purity Yb was about 90% complete becoming 100% or very close when warming up to 250–300°K. The

diamagnetism could be kept at 300°K at least for several weeks without a noticeable change in susceptibility.

The conversion of about 0.8%  $\text{Yb}^{3+}$  into  $\text{Yb}^{2+}$  involves a volume expansion because the  $\text{Yb}^{2+}$  has a larger atomic volume compared to  $\text{Yb}^{3+}$ , and our thermal-expansion measurements yield  $\Delta V/V = (2.3 \pm 0.1) \times 10^{-3}$  at the transition. From the lattice constants at room temperature  $\Delta V/V$  is found to be  $0.91 \times 10^{-3}$  only, in poor agreement with the thermal-expansion results. The x-ray lines were very spotty especially in the hcp phase and, therefore, the x-ray value cannot compete in accuracy with the thermal-expansion measurements.

We can calculate the magnetic part of the expansion  $\Delta V/V$  in an alternative way from the number of trivalent ions determined from the temperature-dependent susceptibility above room temperature:

$$\Delta V/V = f(V_{\text{Yb}^{2+}} - V_{\text{Yb}^{3+}})/V_{\text{Yb}^{2+}}. \quad (2)$$

We find  $V_{\text{Yb}^{2+}} = 24.89 \text{ cm}^3/\text{mole}$  from the hcp lattice parameters (fcc would yield  $24.87 \text{ cm}^3/\text{mole}$ ) and  $V_{\text{Yb}^{3+}}$  was interpolated from neighboring elements to be  $18.0 \text{ cm}^3/\text{mole}$ . With  $f = 8.6 \times 10^{-3}$ , expression (2) yields a value of  $2.38 \times 10^{-3}$  for  $\Delta V/V$ , in good agreement with the experimentally determined  $\Delta V/V$  from thermal-expansion measurements. In general, (2) cannot be expected to yield identical results as compared to the experimentally determined value of  $\Delta V/V$ . From the close agreement, however, it is tempting to speculate that the driving force of the phase transition could be the small fraction of  $\text{Yb}^{3+}$  which will have its  $4f$  holes filled in the hcp phase. The close agreement at least lends substantial support to the model we have presented to explain the magnetic behavior. A second, even

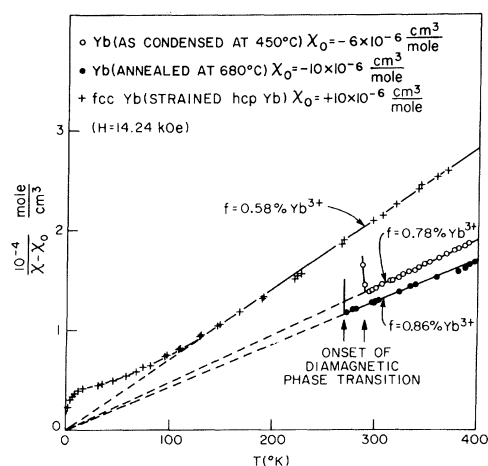


FIG. 4. Plot of  $1/(\chi - \chi_0)$  versus temperature for the same samples shown in Fig. 2.  $\chi_0$  is the background susceptibility obtained by plotting  $\chi$  versus  $1/T$  and assumed to be temperature independent.

stronger, argument for the model comes from the observed and calculated entropy change  $\Delta S$  associated with the transition. For our first-order phase transition, the entropy change  $\Delta S$  is given by

$$\Delta S = L/T = \Delta V/(dT/dP) = f \times R \ln(2J+1). \quad (3)$$

The left-hand side  $\Delta V/(dT/dP)$  was found to be  $0.128 \text{ J}/^\circ\text{K mole}$  from thermal-expansion measurements and the pressure dependence of the magnetic transition, while the right-hand side  $f \times R \ln(2J+1)$  was determined as  $0.134 \text{ J}/^\circ\text{K mole}$  from magnetic measurements alone. The agreement is very satisfactory and seems to indicate that the volume change between fcc and hcp phase is indeed mainly due to the conversion of  $\text{Yb}^{3+} \rightarrow \text{Yb}^{2+}$ . It may be concluded further that any volume difference due to the change in electronic structure must be much smaller than our measured values.

Our resistivity measurements yield further independent evidence for the bulk nature of this magnetic phase transition. At the onset of the transition we found a drop in resistivity. It shows the same degree of hysteresis as the magnetic susceptibility when cooling down to  $160^\circ\text{K}$  and warming up to above room temperature. The total drop  $\Delta\rho/\rho$  shown in Fig. 3 amounts to about 23–25% in various samples. Our results are similar to those recently reported by Kayser and Soderquist.<sup>16</sup> Neither x-ray studies nor magnetic measurements have been reported by these authors, but they found that gas contamination removed the anomaly. In contrast, our samples, exposed to air for variable lengths of time, showed reproducible magnetic properties.

Although the contributions to the resistivity change cannot be separated, the drop in resistivity at the transition is at least qualitatively consistent with our model. If the  $4f$  moments are lost in the para-to-diamagnetic transition, the spin-disorder contribution to the resistivity would vanish, resulting in a drop in resistivity.

In Fig. 2 we show the temperature-dependent susceptibility of fcc Yb obtained by plastically deforming a condensed high-purity sample which exhibited the magnetic transition and diamagnetism down to liquid-helium temperatures. The temperature dependence of  $\chi$  is again analyzed on the basis of Eq. (1). We find  $\theta \approx 0$ ,  $f \approx 0.58 \times 10^{-2}$ , and  $\chi_0 = +10^{-5} \text{ cm}^3/\text{mole}$ . This very definitely excludes any impurity effects in fcc Yb on which suspicion was cast in connection with Lock's measurements.<sup>11,17</sup> We would like to point out, however, that his analysis of his data is incorrect. He used for  $\chi_0$  the value of La which is far too large, thus yielding too small a number for  $f$ . Furthermore, crystal-field effects were neglected in Ref. 9. In Fig. 4 we find a Curie law down to about  $130^\circ\text{K}$ , suggesting again that crystal-field and exchange effects are negligible above this temperature. Below  $130^\circ\text{K}$ , crystal-field

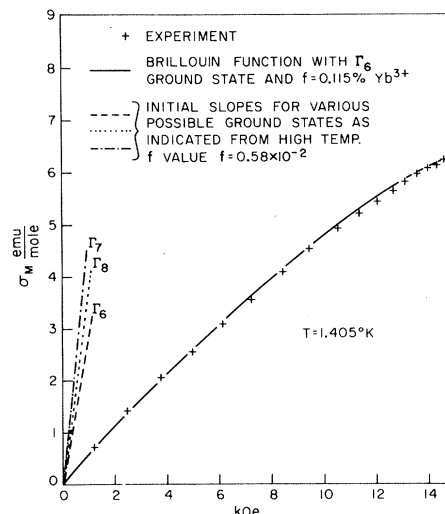


FIG. 5. Magnetization versus field for hcp Yb at  $1.405^\circ\text{K}$ .

splitting effects could qualitatively account for its behavior. The situation must be much more complex however. In Fig. 5 we show the magnetization curve at  $1.405^\circ\text{K}$  in fields of up to 15 kOe. Shown also are calculated initial slopes of the magnetization curve for the various ground states which are possible in a crystal field of octahedral symmetry, based on the assumption that  $f = 0.58 \times 10^{-2}$  remains constant and that the  $\text{Yb}^{3+}$  ions interact only with the applied field (i. e., neglecting exchange effects). The magnetization curve fits a Brillouin function for a  $\Gamma_6$  ground state reasonably well, which is most likely the ground state in fcc Yb.<sup>18</sup> The fit, however, is only possible if we assume that  $f$  dropped by a factor of exactly 5 from about  $130^\circ\text{K}$ . This seems to indicate that we lose a considerable fraction of the  $\text{Yb}^{3+}$  by gradual conversion to  $\text{Yb}^{2+}$  by cooling to below  $130^\circ\text{K}$ . No hysteresis, however, was detectable in this process by warming and cooling again. The gradual conversion of  $\text{Yb}^{3+}$  into  $\text{Yb}^{2+}$  below  $130^\circ\text{K}$ . No hysteresis, however, was detectable in this process by warming and cooling again. The gradual conversion of  $\text{Yb}^{3+}$  into  $\text{Yb}^{2+}$  below  $130^\circ\text{K}$  should be detectable by thermal-expansion analysis; otherwise a more powerful tool for a microscopic analysis such as Mössbauer effect, NMR, or possibly EPR is needed to bring some light into this puzzle.

As mentioned in Sec. II C the low-temperature resistivity of fcc Yb was found to vary as  $T^{2.50}$  between 1 and  $15^\circ\text{K}$ . As usual for transition elements, such a power law means that we have terms proportional to  $T^2$  and to  $T^5$ , the former being characteristic for  $s$ - $d$  scattering processes. The conclusion from resistivity measurements alone is not very convincing since we do not know exactly whether the fraction  $f$  of  $\text{Yb}^{3+}$  (and therefore the spin-disorder contribution) remains constant within this temperature range. Some support, however, for the existence of the  $T^2$

term arises from the specific-heat measurements. The linear term  $\gamma$  was found to be quite high and field independent in fields of up to 106 kOe. It might seem, therefore, that our large  $\gamma$  value is not due predominantly to a magnetic contribution, as, e.g., suggested by Marshall's analysis of a dilute system of disordered spins.<sup>14,15</sup> We would like to emphasize, however, that our specific-heat results raise two new problems. If the field-independent linear term  $\gamma$  is interpreted as a density of states, one would expect a far higher background susceptibility  $\chi_0$  than  $10 \times 10^{-6}$  cm<sup>3</sup>/mole. Otherwise, one has to assume an extremely large Landau term and/or a strongly temperature-dependent density of states decreasing rapidly with increasing temperature. Gossard and co-worker's<sup>11</sup> temperature-independent Knight-shift results are strongly against the latter assumption. This difficulty could indicate that we may possibly have an additional linear specific-heat term arising from fluctuation effects between the two valence states of Yb. The second problem is an even more serious one. From Fig. 6 we can evaluate experimentally the area between the specific-heat curves at 0 and a field  $H$  of 106 kG. It is a simple matter to show by standard statistical thermodynamics that

$$\int_0^\infty \frac{C(H) - C(O)}{T} d(T^2) = 2fN g_J \mu_B J_{\text{eff}} H \quad (4)$$

for  $fN$  noninteracting Yb<sup>3+</sup> ions being in a Kramers doublet ground state characterized by  $J_{\text{eff}}$ . For a  $\Gamma_6$  ground state, which we may expect,<sup>18</sup> we have  $J_{\text{eff}} = \frac{7}{6}$  while  $f$  is taken from Fig. 4. Equation (4) yields a theoretical value of  $+1.8 \times 10^6$  erg/mole, while from Fig. 6 we evaluate the integral to be  $-9 \times 10^4$  erg/mole, i. e., a discrepancy of a factor of 20, and even the wrong sign which is far beyond experimental error. (Of course if one would consider the entropy, the discrepancy is exactly the same.) It is explicitly assumed, of course, that the electronic and lattice contributions to the specific heat are field independent. The conclusion we can draw is that our assumption of  $fN$  individual Yb<sup>3+</sup> ions/mole being in a Kramers doublet ground state and interacting with the external field is wrong only because there is no evidence that the electronic and lattice specific heat are field dependent. (It is clear that the assumption of other than a  $\Gamma_6$  ground state will only increase the discrepancy.) On the other hand, there is no evidence for a strong exchange coupling between the  $4f$  moments. The solution of this problem has to await more experimental results about the nature of the  $4f$  electron system in Yb metal.

#### IV. CONCLUSIONS

Unstrained high-purity Yb metal exhibits three crystallographic modifications: bcc between 660 °C and the melting point ( $\sim 823$  °C), fcc between 660 °C

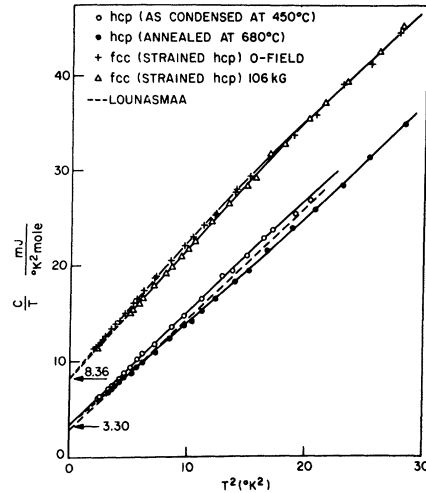


FIG. 6. Specific heat  $C/T$  versus  $T^2$  for hcp Yb[as-condensed and annealed and fcc Yb (obtained by plastic deformation of hcp Yb) at 0 and 106 kOe].

and room temperature, and hcp at low temperature. The fcc $\rightarrow$ hcp transition exhibits characteristics of a martensitic transformation with a large degree of hysteresis. The onset occurs abruptly at 0–20 °C when cooling and at 40–45 °C when warming. The transformation rate and onset temperature depends strongly on purity, internal stress, and pressure, and is very sluggish within about 0–45 °C. The hcp $\rightarrow$ fcc conversion is complete at about 150 °C when warming up. When cooling, the reverse transformation is only about 90% complete at 77 °K (at a cooling rate of about 2°/min), but can be made 100% complete when warming back to room temperature. The onset of transformation when cooling drops at a rate of 45°/kbar. Plastic deformation destroys the hcp phase in any case, by either converting it to fcc or by suppressing the martensitic transformation.

The magnetic behavior, thermal expansion, and other results are consistent with a model which assumes the presence of a fraction of 0.8–0.9% Yb<sup>3+</sup> in the unstrained fcc phase. The fcc $\rightarrow$ hcp transformation is coupled with the conversion of this fraction of Yb<sup>3+</sup> into Yb<sup>2+</sup>, leading to a temperature-independent diamagnetism of  $(-27.1 \pm 0.5)10^{-6}$  cm<sup>3</sup>/mole in the hcp phase. The presence of Yb<sup>3+</sup> in the fcc phase is therefore an intrinsic property of this phase and excludes impurity effects. Plastic deformation at room temperature results in a fairly constant amount of  $\sim 0.6\%$  Yb<sup>3+</sup> at least down to 130 °K. Below, there is a gradual reduction of the apparent number of Yb<sup>3+</sup> which drops to 0.12% at 1.4 °K.

The conversion of Yb<sup>3+</sup> $\leftrightarrow$ Yb<sup>2+</sup> involves a small volume change and, therefore, the fcc $\leftrightarrow$ hcp transition must be of first order, which is also demonstrated by the hysteresis effect. Using standard thermo-

dynamics, it can be shown that the volume difference between hcp and fcc Yb is mainly due to this valency conversion, i. e., other effects being at least an order of magnitude smaller, and, therefore, cannot be separated out.

In hcp Yb we measure an electronic specific heat  $\gamma = 3.30 \pm 0.1 \text{ mJ}/^\circ\text{K}^2 \text{ mole}$ ,  $\Theta_D = 117.6^\circ\text{K}$ , in agreement with previous measurements by Lounasmaa. The latter author attributed these values to the fcc phase. According to our magnetic measurements on his sample, his parameters apply to the hcp phase.

For the fcc phase that we obtained by plastic deformation of the hcp Yb, we measure a field-independent  $\gamma = 8.36 \text{ mJ}/^\circ\text{K}^2 \text{ mole}$  and  $\Theta_D(0) = 109^\circ\text{K}$  in 0 field and  $113^\circ\text{K}$  at 106 kOe. A field of 106 kOe at liquid-He temperature is ineffective in reducing the spin-disorder entropy. The specific heat is only slightly field dependent below  $4.5^\circ\text{K}$ .

We did not observe any evidence either for superconductivity of the diamagnetic hcp phase down to  $0.015^\circ\text{K}$  or magnetic ordering of the fcc phase down to  $1.0^\circ\text{K}$ .

There are quite a few puzzles unsolved with regard to Yb. What is the stability region of the hcp phase in a  $P$ - $T$  diagram? The ease with which hcp transforms to fcc indicates that the stacking-fault energy is very low. The next question is how are the  $\text{Yb}^{3+}$  locally distributed in the phase, or are the  $4f$  holes even itinerant?<sup>14</sup> Is the presence of stacking faults necessary for creating  $\text{Yb}^{3+}$  or does the presence of excess stacking faults suppress the  $\text{Yb}^{3+}$  to  $\text{Yb}^{2+}$  transition? At present we have no answers to these questions.

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<sup>14</sup>Note added in proof. Professor J. Friedel suggested (private communication) that in fcc Yb the  $4f$  levels may be resonance broadened by conduction electrons. They

would be only partly filled and therefore be itinerant in nature. This idea seems to be particularly convincing with regard to Fig. 6, and the continuous loss in  $4f$  magnetism below  $130^\circ\text{K}$  could be explained by a temperature-dependent  $4f$  density of states. The fact, however, that all the thermodynamic relations are perfectly fulfilled leads us to the assumption of well-localized  $4f$  states in this phase. Recently, the existence of this phase transition has also been reported by F. X. Kayser [*Phys. Rev. Letters* **25**, 662 (1970)] and S. Tanuma, W. R. Datars, H. Doi, and A. Dunsworth [*Solid State Commun.* **8**, 1107 (1970)].

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