POLYMORPHIC TRANSFORMATION IN YTTERBIUM*

F. X. Kayser
Institute for Atomic Research and Department of Metallurgy, Iowa State University, Ames, Iowa 50010
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The purpose of this Letter is to report the discovery of a polymorphic transformation in Yb and to provide a brief discussion of its significance in relation to recent high-pressure studies. The transformation, $\beta(\text{fcc}) \leftrightarrow \alpha(\text{hcp})$, is martensitic, the α phase being the stable form at 1 atm below ~270°K. The slope of the α/β equilibrium boundary, $(dT_{\alpha,\beta}/dP)_{270°, 1\,\text{atm}}$, is (-23 ± 8)°K/kbar.

Experiments performed on high-purity annealed polycrystalline specimens of Yb at 1 atm have shown that the stable room temperature form, β(fcc), transforms on cooling to α(hcp).[1] The transformation, which is martensitic, starts on cooling at ~260°K. Under favorable conditions specimens can be converted to ~90% α-Yb. The transformation is readily reversible on heating; for example, it begins at approximately 280°K and is completed at (365 ± 15)°K. The temperature, $T_{\alpha,\beta}$, at which bulk strain-free quantities of the two phases would be in thermodynamic equilibrium under a given pressure is estimated to be 270°K at 1 atm. Lattice parameters were determined from specimens at 296°K by x-ray-diffraction methods. They were (i) for β (fcc), $a_0 = 5.4847 \pm 0.0002$ Å and (ii) for α(hcp), $a = 3.8799 \pm 0.0002$ Å and $c = 6.3859 \pm 0.0002$ Å. The diffusionless character of the transformation, coupled with a near-perfect correspondence of linear dimensions in the planes $(111)_\beta : (0001)_\alpha$, suggests that it is of the stacking-fault type analogous to the fcc $\to$ hcp transformation in Co.

A hysteresis is expected in any macroscopic property of a Yb specimen that is being cycled through the transformation. This is true irrespective of whether the conditions are isothermal, isobaric, or mixed. Figure 1 illustrates a hysteresis in the electrical resistivity as measured at 1 atm. The upper branch represents the resistivity of β-Yb, ρ_β. It was found to be linear over the temperature range 260 to 450°K. The thermal component of resistivity for this branch could not be fitted by the Bloch-Grüenisen relation; at least, not under the usual assumptions that (i)

$$\lim_{T \to 0} (\rho_\beta) \to 0,$$

and (ii) the resistivity-derived Debye temperature is either a constant or a weak function of the temperature.[2] This is also evident from the fact that the linear extrapolation to 0°K of the ρ_β data line yields an extraordinarily high value. The lower branch in Fig. 1 represents the resistivity after the specimen had been converted to ~90% α-Yb. The thermal component of resistivity for this branch was well described by the Bloch-Grüneisen relation.[1]

Nearly a dozen independent investigations have been made of the behavior of Yb under pressure.[3-6] Since the results of all but one of these were published without knowledge of the above-noted polymorphic transformation,[5] it is important to inquire into the effect it might have had on the results.

We begin with the calculation of $(dT_{\alpha,\beta}/dP)_{270°,1\,\text{atm}}$. The form of the Clausius-Clapeyron equation for the $\alpha \to \beta$ transformation at 1 atm is $dT_{\alpha,\beta}/dP = 270°(v_\beta - v_\alpha)/l$, where l, the latent heat of transformation, is positive. We have $v_\beta - v_\alpha = -0.00123$ cm^3/g and an estimate (from an analysis of published specific-heat data) that $0.26 < l < 0.52$ cal/g.[1] Substitution yields $(dT_{\alpha,\beta}/dP)_{270°,1\,\text{atm}} = (-23 \pm 8)$°K/kbar. Most, and perhaps all, of the boundary $T_{\alpha,\beta}$ in the PT plane should lie within the region bounded by the linear extrapolation of the extremes. This information has been added to the PT diagram for Yb as indicated in Fig. 2.[3,4]

The only way to obtain a 100% α-Yb specimen would be to induce the $\beta \to \alpha$ transformation in a single crystal of β-Yb. Even here some rather

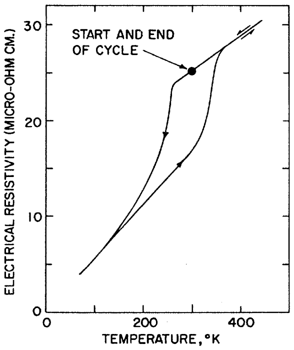

FIG. 1. The electrical resistivity of a Yb specimen that was cycled at $P = 1$ atm. The specimen transformed to ~90% α-Yb.

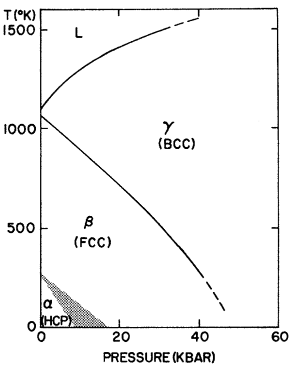

FIG. 2. Pressure-temperature diagram for Yb. Boundaries $T_{L,\gamma}$ and $T_{\beta,\gamma}$ are taken from Ref. 4. All or most of the boundary $T_{\alpha,\beta}$ should lie within the shaded region.

special procedures might be required. All of the experimental work referenced or reported in this paper was conducted on polycrystalline specimens. A net effect of perturbations resulting from the use of such material is demonstrated in the following experiment. Imagine a series of annealed polycrystalline β-Yb specimens at 300 °K, the individual members of which are placed under true and reversible hydrostatic pressures like 1 atm, 1 kbar, •••, 20 kbar. Under isobaric cooling certain of these will begin to transform to α-Yb. The locus of the pressure/start-of-transformation temperature points will comprise a curve which will lie somewhere below $T_{\alpha,\beta}$ in the PT plane. The former curve is commonly called $M_s^{\beta\rightarrow\alpha}$.[7] The question is, "When these specimens are cooled to some temperature $T_i < 260$°K, how will the volume fraction of α at this temperature, $f_\alpha(T_i)$, vary with the pressure?" It will vary in a continuous manner, becoming zero valued at a pressure just greater than the intercept of the $M_s^{\beta\rightarrow\alpha}$ curve at T_i. Some recent data suggest that at 4.2°K the intercept in question occurs at either 10 or 14 kbar.[6] Additional considerations[8] indicate that $f_\alpha(T_i)$ should be maximum valued at low pressures. The resulting f_α-versus-P curve at, for example, 4.2°K should be qualitatively similar to those in Fig. 3(a). Its form will be such that if one measured some macroscopic property φ of these specimens at T_i, no discontinuity would be observed in the graph of $\varphi(P)$ at the pressure corresponding to the $M_s^{\beta\rightarrow\alpha}$ intercept.

We now return to the question of how the $\beta\rightarrow\alpha$ transformation has manifested itself in high-pressure studies. The discussion is restricted to results obtained by Jerome and Rieux during a recent search for a pressure-induced metal-to-insulator transition in Yb.[6] Their data were obtained under conditions similar to those detailed in the preceding paragraph.[9] The several specimens examined by them (i) evidenced good behavioral reproducibility in the temperature and pressure range of interest here, and (ii) had resistivity ratios indicative of a purity sufficient for realization of the $\beta\rightarrow\alpha$ transformation.[10]

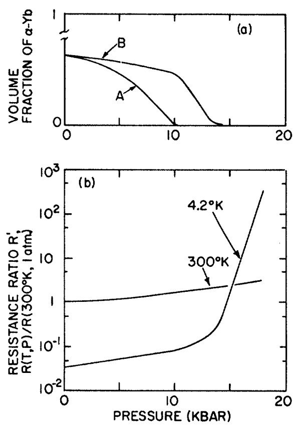

FIG. 3. (a) Several possible representations of the volume fraction of α-Yb at 4.2°K in isobarically cooled polycrystalline specimens. (b) The resistance ratio R' of isobarically cooled polycrystalline specimens as measured by Jerome and Rieux, Ref. 6.

Figure 3(b) is a representation of the Jerome and Rieux resistance-ratio data, $R' = R(T,P)/R(300°\mathrm{K}, 1\ \mathrm{atm})$. The curve obtained with the specimens at 300°K presents no problems. It is clear, with reference to Fig. 2, that these measurements were made on β-Yb specimens. One can make the following comments with regard to the 4.2°K data. They appear to demonstrate an effect associated with the presence of α-Yb. Unfortunately, a unique correlation of structure and resistivity cannot be provided without explicit knowledge of the volume fraction of α-Yb in these specimens. The two most likely correlations are related to the curves of Fig. 3(a) and are as follows:

(1) $f_\alpha(4.2°\mathrm{K})$ is as indicated in curve A, in which case the behavior for $P \gtrsim 10$ kbar is characteristic of β-Yb. The residual resistivity of the β phase then appears to extrapolate to a value at $P = 1$ atm typical of an elemental metal in a nonsuperconducting state.

(2) $f_\alpha(4.2°\mathrm{K})$ is as indicated in curve B, whose three segments, and their counterparts in the $\ln R'$ vs P curve, correspond to the approximate pressure intervals 0 to 10, 10 to 14, and 14 to 17 kbar. A positive-valued $d^2\ln R'/dP^2$ in the

middle interval coincides with the rapid decay of f_α to zero. The linear segment at high pressures reflects a genuine property of β-Yb. Although the extrapolation of this segment to low pressures is indefinite, it does portend a low residual resistivity for β-Yb at $P=1$ atm.

In order to provide an unambiguous explanation for data like those obtained by Jerome and Rieux at 4.2°K and at pressures below ~14 kbar several experiments are necessary. One is a determination of the boundary $T_{\alpha,\beta}$ and the other is a study of the effect of pressure on the electrical conductivity of α-Yb.

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[1] F. X. Kayser and E. D. Gibson, to be published. The designations fcc and hcp signify face-centered cubic and hexagonal close-packed crystal structures, respectively.

[2] The occurrence of ferromagnetism or antiferromagnetism at low temperatures in β-Yb is considered unlikely. See also D. B. McWhan, T. M. Rice, and P. H. Schmidt, Phys. Rev. 177, 1063 (1969), on this point.

[3] A. Jayaraman, in *Physics of Solids at High Pressures,* edited by C. T. Tomizuka and R. M. Emrick (Academic, New York, 1965), p. 478.

[4] W. Klement and A. Jayaraman, in *Progress in Solid State Chemistry,* edited by H. Reiss (Pergamon, Oxford, England, 1967), Vol. 3, p. 289.

[5] McWhan, Rice, and Schmidt, Ref. 2.

[6] D. Jerome and M. Rieux, Solid State Commun. 7, 957 (1969).

[7] Literally, $M_s^{\beta\rightarrow\alpha}$ signifies the temperature at which the martensitic $\beta\rightarrow\alpha$ transformation starts on isobaric cooling (or the pressure at which it starts on isothermal decompression). For a thermodynamic justification of the necessity for undercooling below $T_{\alpha,\beta}$ in order to start the transformation on cooling see, for example, J. W. Christian, *Transformation in Metals and Alloys* (Pergamon, Oxford, England 1965), Chap. XXIII.

[8] External pressure has several effects on the kinetics of the transformation. The first two arise from the existence of a two-phase aggregate. Even in the absence of an external pressure, the rigid coherence along interfaces (habit planes) of discrete volumes of two elastically unique phases, combined with $v_\beta - v_\alpha \neq 0$, will give rise to complex internal nonhydrostatic stress fields. The shear components of these acting on appropriate β-slip planes will reduce the activation energy for the nucleation of transformation dislocation loops, thereby enhancing the nucleation frequency. This is the basis of the autocatalytic nature of martensitic transformations. External hydrostatic pressure will increase the intensity of these shear stress fields and, if this reasoning is correct (and a third effect below is neglected), tend to improve the kinetics in the early stages of transformation. Since it does so by increasing the nucleation frequency, the untransformed portion of the crystal will rapidly be partitioned into isolated volumes which will be resistant to transformation. The latter will act to retard the rate of transformation in the later stages. A third effect is related to the negative value of $dT_{\alpha,\beta}/dP$. Depressing the temperature range for the transformation reduces the thermal energy available for assisting in the nucleation of transformation dislocations. This will act to retard the transformation. The combination of these effects should produce $f_\alpha(T_i)$ vs P curves like A or B in Fig. 3 (a). B differs from A only in the greater weight given to the first effect above.

[9] D. Jerome, private communication.

[10] The significance of the resistivity ratio is obscure in instances where a phase transformation occurs between 300 and 4.2°K. We have, however, amassed a background of information that is useful in determining whether or not a significant amount of α-Yb will form on cooling. Thus, if the ratio of the electrical resistance of a freshly annealed specimen at 300°K to its resistance at 4.2°K is 15, 25, or 100, this corresponds roughly to 25-, 50-, and 90-vol.% α-Yb, respectively. The two specimens of Jerome and Rieux had ratios of 15 and 30. The displacement of their R' curves at 4.2°K may be related to differences in $f_\alpha(4.2°\mathrm{K})$.