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Canadian Journal of Physics

Réimpression du

Journal canadien de physique

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Volume 52 • Number 17 • 1974

Pages 1622–1627

National Research Council Canada

Conseil national de recherches Canada

Pressure Dependence of the de Haas – van Alphen Effect in Ytterbium[1]

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Received February 18, 1974

The de Haas–van Alphen effect and the h.c.p.–f.c.c. phase transformation of ytterbium were studied with the magnetic field along the [0001] direction in the h.c.p. phase, using pressures up to 4 kbar. Solid helium was used as the pressure medium. The pressure dependence of the three dHvA frequencies in the h.c.p. phase for the [0001] magnetic field direction was linear within experimental error with $dF/dP = -1.2 \pm 0.2$ T/kbar for $F(P = 0)$ of 35.4 T, $dF/dP = 0.30 \pm 0.03$ T/kbar for $F(P = 0)$ of 142.5 T, and $dF/dP = -0.78 \pm 0.10$ T/kbar for $F(P = 0)$ of 156.4 T. The dHvA amplitude in the h.c.p. phase was independent of pressure up to the phase transition and no dHvA effect was observed in the f.c.c. phase. The pressure of the phase transformation at 1.2 K was determined to be 2.15 ± 0.05 kbar.

L'effet de Haas–van Alphen et la transformation de phase h.c.–c.f.c. de l'ytterbium ont été étudiés avec un champ magnétique suivant la direction [0001] de la phase h.c. et en utilisant des pressions allant jusqu'à 4 kbar, avec l'hélium solide comme médium de pression. La variation en fonction de la pression des trois fréquences dHvA dans la phase h.c., pour la direction [0001] du champ magnétique est linéaire, dans les limites d'erreur expérimentale, avec $dF/dP = -1.2 \pm 0.2$ T/kbar pour $F(P = 0)$ de 35.4 T, $dF/dP = 0.30 \pm 0.03$ T/kbar pour $F(P = 0)$ de 142.5 T et $dF/dP = -0.78 \pm 0.10$ T/kbar pour $F(P = 0)$ de 156.4 T. L'amplitude dHvA dans la phase h.c. reste indépendante de la pression jusqu'à la transition de phase, et aucun effet dHvA n'est observé dans la phase f.c.c. On a trouvé pour la pression de transformation de phase à 1.2 K la valeur 2.15 ± 0.05 kbar. [Traduit par le journal]

Can. J. Phys., **52**, 1622 (1974)

1. Introduction

The polymorphic f.c.c.–h.c.p. transformation in Yb first observed by Kayser and Soderquist (1969) has been documented by Kayser (1970), Bucher *et al.* (1970), and Rieux and Jerome (1971). At a pressure of 1 atm, the transition commences just above room temperature with an increasing fraction of the h.c.p. phase being produced as the temperature is lowered. The sample reverts to the f.c.c. phase below room temperature under sufficient applied pressure. The boundary delineating the start of the transformation to the h.c.p. phase is shown by the phase diagram determined by Rieux and Jerome (1971) in Fig. 1. Some mixture of the two phases is found to the left of and below this boundary; only the f.c.c. phase exists to the right and above.

The band structure of Yb has been calculated by the relativistic augmented plane wave (APW) method for both the f.c.c. and h.c.p. phases. Face centered cubic ytterbium is predicted to be a semiconductor with the Fermi energy at normal pressure lying in an *sp–d* hybridization gap (Johansen and Mackintosh 1970; Jepsen 1971). Calculations for the h.c.p. phase show two second-band hole surfaces and three third-band electron surfaces (Jepsen and Andersen 1971).

Ytterbium was the first rare earth element to be investigated by the de Haas – van Alphen (dHvA) effect (Tanuma *et al.* 1967). Measurement of dHvA frequencies in the h.c.p. phase showed a set of low frequencies in the range 0.1 to 1 MG for all field directions and two higher frequencies in the region of the [0001] axis (Tanuma *et al.* 1970). These frequencies were assigned to orbits of the Fermi surface by Jepsen and Andersen (1971). However, some of these assignments are tentative and the Fermi surface of ytterbium requires more experimental and theoretical considerations.

The magnetic field direction chosen for this study was the h.c.p. [0001] direction where there are three dHvA oscillations with large amplitude. This direction also has the advantage that the frequencies change slowly with magnetic field direction so that small misalignment is not a serious problem. X-ray studies indicated that a single h.c.p. crystal is formed from a single

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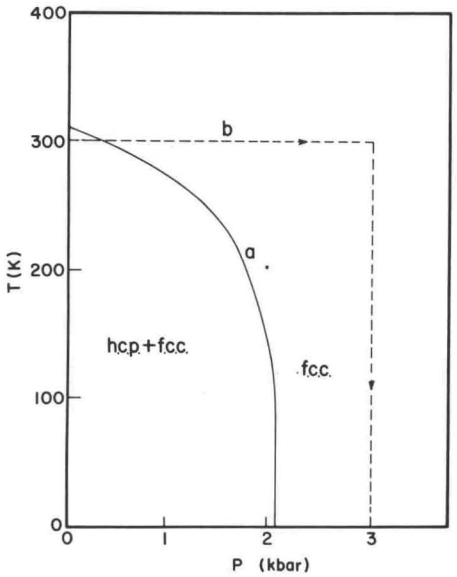

FIG. 1. The solid line a shows the start of the h.c.p. phase of Yb on a *PT* diagram. The dashed line b indicates the path followed in one experiment to form a f.c.c. crystal at 1.2 K.

f.c.c. crystal during cooling and it was hoped that the pressure induced transformation to the f.c.c. phase at low temperatures would again create a single crystal.

The present work was undertaken to measure the pressure dependence of dHvA frequencies for the h.c.p. phase, to look for the dHvA effect in the f.c.c. phase, and to study the h.c.p.–f.c.c. transformation at low temperatures using the dHvA effect. This is the first report of an attempt to observe the dHvA effect on both sides of a polymorphic transition and to study the transition itself by the dHvA effect. The dHvA effect is very useful for such a study because the crystal phase can be identified by the symmetry of the angular dependence of frequency, and the dHvA amplitude depends on the amount of the phase that is present. The pressure dependence of the dHvA frequencies can be compared directly with theoretical calculations. Such calculations are being carried out for Yb by Jepsen and Andersen (private communication).

Details of our high pressure system are described in this paper. Helium is used as the pressure transmitting medium to apply pressures up to 7 kbar. The high pressure cell with electrical feedthroughs for the dHvA measurements is also described.

II. Experimental Method

Pressures up to 7 kbar were obtained using a Harwood Engineering[3] Portable Pressure Generating System modified for use with gases by the addition of a 1:1 gas/oil separator which acted as a charge pump for the intensifier. The system is similar to the 9 kbar system described by Schirber (1970). Helium was used as the pressure transmitting medium, and was transferred from the pressure generating system to the dHvA pressure cell by a stainless steel capillary.

The pressure cell was constructed of beryllium copper, heat treated to a Rockwell hardness of Rc 42. In initial experiments, the modulation, pickup, and balanced coils required for the dHvA measurements were wound on the exterior of the cell to avoid the problems of making high pressure electrical feedthroughs. Unfortunately, the filling factor of the sample in the pickup coil was too small using this construction, resulting in a signal-to-noise ratio of only 5 at 5 T and 1.2 K. Therefore, a cell was made with the pickup and balance coils inside the cell and only the modulation coil on the exterior. This gave a signal-to-noise ratio of about 500. The electrical feedthrough was similar in design to that described by Schirber and Shanfeldt (1968). It was constructed using four-conductor ceramically insulated thermocouple wire, sealed against gas leaks with an alumina-filled epoxy resin, which had been outgassed before being applied to the high-pressure side of the feedthrough. This seal was cured *in situ* in the bomb at 1.5 kbar to force the epoxy into the powdered insulation. At slightly higher pressures, the epoxy became jelly-like and would not cure until the pressure was reduced. It was important to use an epoxy with an expansion coefficient similar to that of metals to avoid leaks upon cooling to liquid helium temperatures. For this reason, the alumina filler was used to decrease the expansion coefficient of the epoxy seal.

All the experiments described here were performed at 1.2 K, at which temperature helium is a solid for pressures above 25 bar. Consequently the helium about the sample was frozen for our measurements under pressure.

[3]Harwood Engineering, Inc. South Street, Walpole, Mass. 02081.

This freezing was carried out under a constant pressure, P_m, for which there was a freezing temperature, T_m. The temperature of the cell was controlled so that helium froze from the bottom of the cell towards the capillary inlet at the top. This was ensured by heating the top of the bomb while transferring cold helium gas (and eventually liquid) below the cell. The temperatures of both ends of the cell were monitored continuously with copper–constantan thermocouples. This method of cooling was chosen, rather than the more common procedure of slowly lowering the apparatus into the dewar containing liquid helium, since it reduced the possibility of unintentional variation of the sample orientation with respect to the magnetic field. The solid helium was cooled at essentially constant volume after the capillary inlet was closed with solid helium. The decrease in pressure on the sample due to contraction of the solid helium was estimated using the data of Spain and Segall (1971) and ignoring the fact that the bottom of the cell was actually slightly below T_m by the time the capillary was frozen. This introduced little error into the final value for the pressure, since the temperature difference between the top and bottom of the cell was typically only about 3 K. The value of the final pressure, P_0, was determined by multiplying P_m by 0.938, obtained by linearization of a plot of P_m as a function of P_0 (Spain and Segall 1971) in the low pressure region.

The pressure P_m was measured using a manganin resistance gauge supplied and calibrated by Harwood Engineering. It was verified that this calibration gave the correct value for the pressure in the cell by measuring the pressure dependence of the superconducting transition temperature, T_c, of a tin sample in the cell and comparing the results with previous work (Jennings and Swensen 1958, and references therein). The measured value of dT_c/dP was $-5.0 \pm 0.4 \times 10^{-2}$ deg/kbar, which agrees with previous work within experimental error.

Typically, only 1 min elapsed between the time the bottom and the top of the bomb passed through the freezing point. This rapid freezing did not cause appreciable nonhydrostatic pressure on a tin sample 7 mm long, since the superconducting transition was found to be very narrow ($\simeq 0.01$ K) and there was no apparent dependence of either transition width or temperature on the freezing time which was varied between 0.5 and 5 min.

The dHvA sample was a single crystal of Yb that had been used in previous dHvA work (Tanuma *et al.* 1970). It was oriented to within 1° of the h.c.p. *c* axis by Laue back reflection photographs, and mounted with epoxy resin to the end of a nylon rod which fitted tightly inside the pickup coil formed to align the *c* axis along the field direction. It was possible that stresses were introduced into the sample because of the different compressibilities of the epoxy mounting glue and the sample, 15×10^{-3} kbar^{-1} and 7×10^{-3} kbar^{-1} respectively. However, the abruptness of the crystallographic transition in Yb (<0.1 kbar) indicated that this was not a serious problem.

The dHvA measurements were made using the modulation method (see review by Stark *et al.* 1968) in fields from 2 to 5 T at 1.2 K, with a modulation frequency of 259 Hz. The detection frequency was restricted to the fundamental of the modulation frequency by the low dHvA frequencies. The dHvA oscillations were recorded on a chart recorder with field markers superimposed every 0.01 T. Simultaneously, the oscillations were digitized and recorded with the corresponding field values on magnetic tape for computer fast Fourier transform (FFT) analysis.

III. Experimental Results

(a) Pressure Dependence of DHvA Frequencies in H.C.P. Phase

The three dHvA oscillations for the [0001] direction were observed in the h.c.p. phase for pressures up to the phase transition. No oscillations were detected with the sample in the f.c.c. phase. The frequency at zero pressure and the derivative of frequency with respect to pressure, dF/dP, are given in Table 1. The errors in F and dF/dP represent ± 2 standard deviations in the intercept and slope, respectively, determined in a least squares linear fit of a plot of F vs. P. The frequencies in the h.c.p. phase will be called by their approximate values, 35 T, 143 T, and 156 T. The methods of determining the pressure dependence of the three frequencies differed and are now discussed briefly.

dF/dP of the 35 T oscillation was sufficiently large that the shift in frequency with pressure could be determined from the FFT analysis of

TABLE 1. The dHvA frequency F at zero pressure and dF/dP for the three frequencies of Yb with the magnetic field along the [0001] direction

$F(P=0)$ (T)	dF/dP (T kbar^{-1})	Method of determination
35.4	-1.2 ± 0.2	Using position of peaks of Fourier transform
142.6 ± 0.3	0.30 ± 0.03	Slope of oscillation no. vs. 1/B plot
156.4 ± 0.4	-0.74 ± 0.15	$dF_2/dP = (dF_1/dP) + (dF_B/dP)$
	-0.74 ± 0.07	First zero crossing
	-0.86 ± 0.06	Second zero crossing

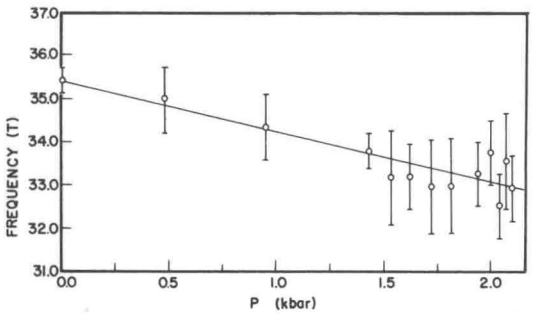

FIG. 2. Pressure dependence of the frequency of the 35 T oscillation of Yb.

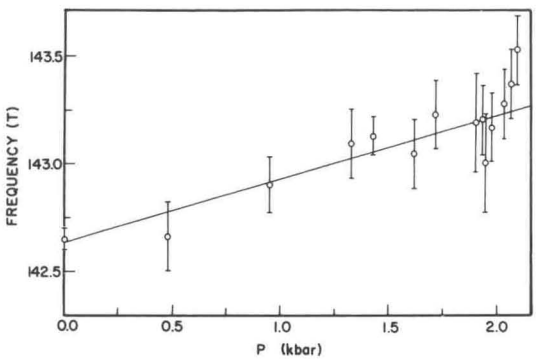

FIG. 3. Pressure dependence of the frequency of the 143 T oscillation of Yb.

the oscillations. The plot of F vs. P is shown in Fig. 2. The error bars in this and the next figure represent ± 2 standard errors as obtained from all data taken at one pressure. (The standard error is $S/\sqrt{N}$ where S is the standard deviation and N is the number of measurements.)

The change in frequency with pressure of the 143 T oscillation shown in Fig. 3 was so small that the change in the position of the peak in the FFT spectrum was less than the uncertainty in the peak position. However, the frequency at each pressure could be obtained accurately from the slope of an n plot given by oscillation number, n, with $n = 0$ arbitrarily assigned, vs. reciprocal field of the oscillation maxima. Although there was some pulling of the oscillation line shape by the signal at 156 T, this effect introduced an error of only 0.03% because the amplitude of the 156 T oscillation was only about 25% of that of the 143 T oscillation and the plots extended over about four beat oscillations.

The results for the 156 T oscillation were obtained using the beat of the 143 and 156 T oscillations. The deviation Δn of n from the least squares line of the n plot exhibited the beat oscillation shown in Fig. 4 because of the

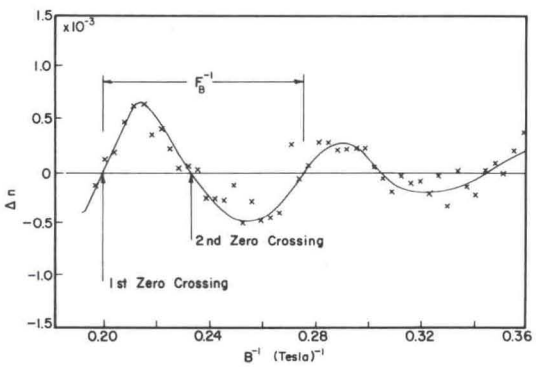

FIG. 4. The deviation Δn from the least squares line of an n plot of the high frequency oscillation of Yb as a function of reciprocal magnetic field.

pulling of the 143 T line shape. A linear fit to a plot of the period $F_B^{-1} = \Delta(1/B)$ vs. pressure gave the zero pressure frequency and dF_B/dP of the beat frequency. These were added to corresponding values for the 143 T oscillation to determine the values for the 156 T oscillation shown in Table 1.

The value of dF/dP for the 156 T oscillation was determined by a second method which

used the pressure dependence of reciprocal field at $\Delta n = 0$. These are the points called zero crossings in Fig. 4. The sum of the two higher frequencies can be written as

$$A_1 \sin(2\pi F_1/B) + A_2 \sin(2\pi F_2/B + \theta)$$

where θ is independent of field and pressure. A zero of Δn occurs when the two signals are in phase or antiphase; that is, whenever

$$[1] \quad \frac{2\pi F_1}{B_c} = \frac{2\pi F_2}{B_c} + n\pi, \quad n = 0, 1, 2, \ldots$$

where B_c is the field value at the zero crossing. Letting $\theta + n\pi = 2\pi\phi$, this becomes

$$[2] \quad F_2 - F_1 = -B_c\phi$$

Therefore

$$[3] \quad \frac{dF_2}{dP} = \frac{dF_1}{dP} - \phi\frac{dB_c}{dP} = \frac{dF_1}{dP} - \left(\frac{F_2 - F_1}{B_c}\right)_{P=0}\frac{dB_c}{dP}$$

The values of dF/dP for the 145 T oscillation determined from [3] for two zero crossings are shown in Table 1. The three values of dF/dP for the 156 T oscillation agree within their combined uncertainties. The uncertainties for dF/dP obtained from the zero crossings is less than for the first method, because the first and second crossings are better defined (large beat amplitude) than is the third crossing used to obtain F_B. The average of the three values is -0.78 ± 0.10 T/kbar.

(b) Transformation to F.C.C. Phase

The amplitudes of the three dHvA oscillations remained constant to within 20% for pressures up to and including 2.10 kbar. No oscillations could be detected at 2.20 kbar and above. The uncertainty in the pressure measurement was about 0.05 kbar. Thus, the pressure of the phase transition at 1.2 K was 2.15 ± 0.05 kbar. This transition region is narrower (<0.1 kbar) than that (≈ 0.5 kbar) observed by Rieux and Jerome (1971) at higher temperatures.

It was established from X-ray diffraction measurements using a beryllium pressure cell that the f.c.c. phase is produced at 300 K with pressures greater than 75 bar. Thus, in an attempt to form a better f.c.c. crystal, the sample was taken into the f.c.c. phase at 1.2 K along the path shown in Fig. 1 in the hope that fewer structural imperfections would be present following a change to the f.c.c. phase at room temperature. For the dHvA experiment, the sample was pressurized to 3 kbar at 300 K for $1\frac{1}{2}$ h and then cooled to 1.2 K over a period of 3 h with the pressure maintained at 3 kbar. No dHvA oscillations were observed in the f.c.c. phase.

Measurements were made at 0.1 kbar intervals close to the phase transition to search for possible effects on the pressure dependence of the dHvA frequency and amplitude close to the phase transition. It was found that the dHvA frequency did not change anomalously at pressures close to the transition but depended linearly on pressure from zero pressure up to the pressure of the phase transition. The amplitude of the dHvA oscillations changed little until they disappeared above 2.10 kbar.

Hysteresis similar to that reported by Rieux and Jerome was observed. Although no extensive study of the hysteresis was made, it was observed that, as the pressure was reduced through the transition pressure, the h.c.p. phase did not reappear by 1.5 kbar but was fully recovered at zero pressure. Rieux and Jerome also report that after several pressure cycles it was impossible to recover the h.c.p. phase without a prolonged anneal at 250 °C. In our experiments no difficulty was encountered in obtaining h.c.p. oscillations, and indeed there was no decrease in amplitude, even after 14 temperature and pressure cycles, including about 10 cycles above the transition pressure at various temperatures.

IV. Discussion

The dHvA frequencies at zero pressure are in agreement with those determined previously by Tanuma *et al.* (1970) to within experimental error. The error of the present values is much smaller because of the large number of measurements that were taken. A good estimate of the uncertainty in the present results introduced by misalignment (less than 1°) of the magnetic field from the [0001] axis is not possible because the exact shape of the frequency branches at [0001] is not known, but it is small because the frequency branches in the region of [0001] change slowly with field direction.

The 35 T oscillation was not assigned to the Fermi surface by Jepsen and Andersen. How-

ever, it is possible that it results from an orbit on the α pocket of electrons. The frequency calculated by Jepsen and Andersen (private communication) for the γ orbit on the cigar-like electron surface centered at K about the HK line is 225 T. This is larger than the 143 and 156 T frequencies but it is reasonable to assign one of them to the γ orbit. The magnitude and sign of the calculated dF/dP for the γ orbit is consistent with our measurements of dF/dP for the 156 T oscillation. This suggests that the 156 T oscillation may be assigned to the γ orbit. The magnitude and sign of dF/dP calculated by Jepsen and Andersen is consistent with the assignment of the 143 T oscillation to the μ' orbit on the hole surface centered at K. However, the calculated dHvA frequency is a factor of 5 too small so that there is no definite evidence for the μ' orbit.

There appear to be four possible reasons for the lack of oscillations above the transition pressure: (*i*) f.c.c. crystallites are nucleating randomly on the four equivalent (111) habit planes, thus averaging the dHvA signal to zero; (*ii*) stacking faults formed during the transition or an admixture of the two phases increase electron scattering to the point where the oscillation amplitude is essentially destroyed; (*iii*) the electrons in the f.c.c. phase have a much larger effective mass (as is usually associated with higher dHvA frequencies) which causes a reduction in amplitude; and (*iv*) the f.c.c. phase is semiconducting as predicted theoretically. Considering these possibilities, (*i*) seems unlikely since the phase formed originally by vapor deposition was in fact f.c.c. and a strong characteristic of martensitic transformations is their reproducibility in transforming from one phase to another and back again. Therefore the sample cooled along path b in Fig. 1 also should have been a single crystal. Thus, it is unlikely that (*i*) and (*ii*) are the cause of no dHvA signal in the f.c.c. phase. Higher field measurements could reveal oscillations if (*iii*) is correct and such experiments are planned for the future. If these oscillations are not found, it is possible that (*iv*) is correct and that the f.c.c. phase is indeed a semiconductor as indicated by the work of Johansen and MacKintosh (1970) and Jensen (1971). This, however, appears to be contradicted by the resistivity measurements of Rieux and Jerome, and Kayser and Soderquist, which show a decrease in resistivity with temperature rather than the increase expected of a semiconducting phase.

Acknowledgments

We wish to thank Dr. S. Tanuma and Mrs. R. Inada for the Yb sample, Dr. S. Minomura for the use of equipment for the X-ray diffraction measurements and for discussions about high pressure techniques, and Dr. S. Tanuma for his continued interest in the work. The research was supported financially by the National Research Council of Canada and by a research grant and a post-doctorate fellowship to A.J.S.

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