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POSITRON ANNIHILATION IN YTTERBIUM METAL TO 80 KILOBARS

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ABSTRACT

Two gamma angular correlation distribution curves from positron annihilation in ytterbium metal were taken at nine different pressures that ranged from 1 atm. to 80 kbar. There was special interest in the region of the fcc to bcc phase transition at 40 kbar. The observed increase in the widths of the measured curves with pressure could be entirely accounted for by the decrease in the volume of the metal with pressure. This indicates that the high pressure (bcc) phase of Yb has only two conduction electrons per atom.

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INTRODUCTION

At atmospheric pressure, Europium and Ytterbium differ from the other Lanthanide metals in that they do not have 5d electron in the ground state of the metal. This difference in electronic structure leads to marked differences in physical properties. It was postulated by Hall, Barnett, and Merrill that Yb reverts to a normal Lanthanide at the 40 kbar phase transition.[5,6] The pressures and temperatures at which Eu may similarly revert are beyond the capabilities of the experimental arrangement in use in this laboratory. Ytterbium, however, can be easily studied, and the discussion is restricted to this metal.

Magnetic susceptibility measurments by Lock indicated that Yb metal has a filled 4f shell and, therefore, can have only two conduction electrons per atom[3]. A typical Lanthanide has three conduction electrons per atom. Ytterbium metal has fair electrical conductivity and the predominant carriers have been shown to be holes[2]. Under ordinary conditions it has a non-typical Lanthanide crystal structure-fcc, unusually low density and high compressibility[1]. In most of its chemical compounds, however, Yb does exhibit typical Lanthanide behavior. It normally forms compounds of Yb^{3+}. It can, however, also form compounds of Yb^{2+}. This latter is not typical behavior for a Lanthanide.

As Yb is subjected to increasingly high pressures, a number of changes occur in its properties[4]. Initially it exhibits an electrical resistivity of about 30 μohm-cm, and a positive temperature coefficient of resistivity. The resistivity rapidly increases with increasing

pressure. Above a pressure of 20 kbar it exhibits a negative temperature coefficient of resistivity. This behavior of the resistivity is not completely understood. There are at least two possible explanations. These are the unlapping of the conduction bands with pressure, and an increase in the resonance scattering of the conduction electrons with pressure. The former explanation is generally accepted. If that explanation is valid, the data indicate that fcc Yb becomes a semiconductor under pressure. The apparent band gap increases with pressure up to about 40 kbar. At that pressure there is a phase transition from fcc to bcc. The bcc phase is metallic in nature. At the phase transition there is about a 3% decrease in volume. Ytterbium then exhibits a typical Lanthanide metallic radius. Basing their conclusions on a hard sphere model, Hall, Barnett, and Merrill postulated that Ytterbium does indeed become a normal Lanthanide after the transition[5,6]. They, therefore, proposed that in the high pressure phase Yb has three conduction electrons per atom. No direct test of this hypothesis had been made up to the work presented herein.

POSITRON ANNIHILATION

An energetic positron which enters a metal is thermalized to room temperature in about 3×10^{-12} sec[7]. Since the lifetime of a positron in a Lanthanide metal is greater than 2×10^{-10} sec[8], it is probable that a positron is thermalized before it annihilates. The ordinarily observed event is the two gamma annihilation.

In simple metals, after the positron is thermalized it has a small probability of penetrating to the atomic cores because of simple

Coulomb repulsion. If the cores are small the positron will annihilate predominantly with conduction electrons. Annihilations with core electrons are more probable in transition metals, and there is usually a considerable background associated with these annihilations. The momentum distribution of the conduction electrons outside the core is adequatly described for the purposes of this experiment by a simple free electron model. That is, the density of states of conduction electrons in momentum space is a constant up to the Fermi momentum, p_F, and zero above it. The Fermi momentum is given by the expression

$$p_F = \hbar(3\pi^2 N/V)^{1/3},$$

where N/V is the density of conduction electrons in real space.

The angular correlation distribution due to the conduction electrons can be calculated if it is assumed that the positron equally samples and does not perturb the conduction electrons. If, as is the normal case, the apparatus can resolve momentum, $\vec{p}$, in one direction only, taken to be the z direction, then the measured angular correlation intensity curve, $I(p_z)$, will be

$$I(p_z) = C(p_F^2 - p_z^2) \quad , p_z < p_F,$$

$$= 0 \qquad\qquad , p_z > p_F,$$

where C is a constant determined by the conditions of the experiment.

$$p_z = mc\Theta, \ \Theta \text{ small},$$

where m is the mass of an electron (or positron), c is the speed of

light, and Θ is the angle between the emitted gamma rays measured in the z direction.

The expected curve is an inverted parabola which goes to zero at the Fermi momentum. A parabola of the expected width has been found for many metals[9-11]. The parabola is invariably superimposed on a broad background. This background is presumably due to annihilations with core electrons. If the number of conduction electrons changes from two to three, as may be expected at the phase transition in Yb, the width of the measured curve will change by a factor of $(3/2)^{1/3}$. This is a change of over 14%.

EXPERIMENTAL

The positron source consisted of about 1.5mCi of "carrier free" $Na^{22}Cl$. This material was placed between two discs of Mylar about 6.5mm in diameter and 0.006mm thick. These Mylar discs were cemented together to form a sealed source. This source assembly was placed between two discs of Yb metal 7.9mm in diameter and 0.18mm thick. The high pressures were applied to this assembly using a set of opposed Bridgman anvils. The anvils had face diameters of 12.7mm. Two pyrophyllite retaining rings each 12.7mm in diameter and 0.254mm high were used to complete the high pressure cell. Electrical leads were admitted between these rings. This made it possible to monitor the electrical resistivity of the sample so that it was known whether or not the transition had occurred. This also served as a secondary check on the pressure.

The angular correlation apparatus was constructed with horizontal slits to take advantage of the small vertical dimension of the sample. The slits were each 0.51mm high and 1.02m from the source. The detectors were 5.1cm NaI(Tl) scintillators.

It is known from previous experience with a source prepared in the same way as the one used here that less than one half of one percent of the non-random coincidences came from within the Mylar and NaCl source material. Also it has been calculated that less than one percent of the coincidences which were detected came from annihilations within the Bridgman anvils. This latter fact results from the large absorption of the gamma rays by the tungsten carbide anvil material. No corrections were made for these two sources of non-random coincidences. The data were corrected for random coincidences and decay of the source. A correction was also made for a small angular dependence of counting rate. This angular dependence results from the fact that some of the gamma rays were blocked by the anvil faces at large angles. None of these corrections exceeded 5%.

RESULTS

Angular correlation curves were taken at nine different pressures from one atmosphere to 80 kbar. It was found that the points taken at angles beyond the central parabolic region could be fit very well by a sum of two Gaussian curves. Gaussian curves were chosen for purely empirical reasons. Points taken beyond about 11 mrad from the center of the distribution were fit with one Gaussian. All the points were corrected for this minor contribution. The corrected points taken

between 6 and 11 mrad from the center were fit with a second Gaussian. All of the points were corrected for this contribution. This was a large correction. The background represented by these two Gaussians is thought to be the result of annihilations with electrons in core states. This background changed very little with pressure. The low angle points, after correcting for this background, could be fit very well with an inverted parabola. The width of this parabola was not strongly dependent on exactly how the background was corrected for.

A typical angular correlation curve is shown in Fig. 1. The dashed curves are the two Gaussians. The lower solid curve is the inverted parabola. The solid curve through the points is the sum of these three curves.

The widths of the fitted curves are shown in Fig. 2 as a function of pressure. Also shown is the predicted behavior of the width. This prediction was based on the free electron theory. Calculated values are shown on the assumption of both two and three conduction electrons per atom. An initial density of 6.98 g/cm^3 for Yb metal was used.[1] The pressure volume data which were used in the calculation are those of Stevens.[12] His data extend only to just past the phase transition at 40 kbar. Two different approximations were used to estimate the density of Yb up to 85 kbar. The upper dashed curve assumes that Yb at 85 kbar has the same density as a normal Lanthanide would have at 45 kbar. This probably overestimates the compressibility because the density of bcc Yb at 40 kbar is still less than that of a normal

Lanthanide at 1 atm. The lower dashed curve assumes that the compressibility of Yb from 40 to 85 kbar is the same as the compressibility of a normal Lanthanide from 0 to 45 kbar. It is felt that this is a more reasonable estimate of the compressibility. Fortunately the Fermi momentum is sufficiently weakly dependent on the volume that it is unambiguous as to whether two or three conduction electrons are present.

DISCUSSION

It is evident from Fig. 2 that this experiment indicates that there are only two conduction electrons per atom in both the fcc and bcc phases of Yb metal. This seems reasonable in retrospect.

The first published postulation of three conduction electrons per atom in the bcc phase appears to have been advanced by Hall, Barnett, and Merrill, who determined the high pressure crystal structure of Yb metal[5,6]. They considered only nearest neighbor distances in comparison of the two crystal structures. They also, evidently, assumed that these distances were determined by the interaction of hard atomic cores. It became necessary for them to propose an unusual mechanism in order to explain the transition from a close packed to a non-close packed structure with increasing pressure. To explain the observed decrease in nearest neighbor distance they proposed that the atomic core had changed. The only rational change appeared to be from a $(Xe)4f^{14}$, 2+ core to a $(Xe)4f^{13}$, 3+ core. The expelled electron would go into either a 5d or 6p conduction band since the 6s band is already full.

This change in the core is not unreasonable. After all, configurations of the type $(Xe)4f^n5d^06s^2$ are the stable configurations of the free atoms for all of the Lanthanides except La, Ce, Gd, Lu, and possibly Tb.[13] Yet, in the metals the stable configurations are of a type $(Xe)4f^{n-1}5d^16s^2$, except for Eu and Yb which tend to maintain a half filled and filled f shell respectively. In most of the Lanthanides, then, the solid state interactions are able to shift the former atomic states enough so that a core with one less f electron than exists in the free atom is stable. The 5d and 6s electrons in the metal are, of course, actually in conduction bands which have nodal properties at the core like d and s electrons.

There are some differences, to be sure, between Yb and a typical Lanthanide such as its neighbor, Tm. Recently Brewer[14] has collated data on the atomic configurations of many elements. The energies of some configurations have been estimated. His work indicates that for an isolated Yb atom the $(Xe)4f^{14}6s^2$ configuration lies 3.1 ± .2 ev below the lowest $(Xe)4f^{13}5d^16s^2$ configuration and 3.9 ± .2 ev below the lowest $(Xe)4f^{13}6s^26p^1$ configuration. In atomic Tm, on the other hand, the lowest $(Xe)4f^{13}6s^2$ configuration is only 1.6265 ev below the lowest $(Xe)4f^{12}5d^16s^2$ configuration and 2.7856 ev below the lowest $(Xe)4f^{12}6s^26p^1$ configuration.[15,16] The energy differences are 1.5 ev greater in Yb than in Tm. This is a large enough difference to suggest the possibility that a 3+ core may not be obtained in Yb metal even though it is obtained in Tm metal.

Hall, Barnett, and Merrill unfortunatly overlooked several other points. One is that although the interatomic distance is over 6a.u.

after the fcc-bcc phase transition, the diameter of a $(Xe)4f^{14},2+$ core probably does not exceed 5a.u. The maximum in the 4f electron distribution in such a core has a diameter of less than 2a.u., and the maximums for the 5s and 5p electrons have diameters of about 3a.u. In its divalent compounds Yb is estimated to have a diameter of about 4a.u.[17] Such a core can still be accomodated in the new crystal structure.

In addition to these facts, the bcc structure may actually be considered to be a more closely packed structure than fcc if a hard sphere model is not used. The fcc structure has 12 nearest neighbors and 6 next nearest neighbors 41% further away. The bcc structure has 8 nearest neighbors and 6 next nearest neighbors only 15% further away. After the phase transition the next nearest neighbors are only 12% further away than the nearest neighbors were in the fcc structure. If next nearest neighbor interactions are important, it no longer becomes necessary to invoke any extraordinary phenomenon in order to explain the transition from a so called close packed structure to a non-close packed structure under the influence of pressure.

This argument is further supported by the remarkable similarities between Yb and Sr metals. These similarities are discussed by Jayaraman.[18] Both metals are face centered cubic at one atmosphere, and they have similar electrical resistivities. The resistivities of both increase an order of magnitude between 1 atm. and 35 kbar. Both appear to be semiconductors above 10 kbar. Strontium assumes a bcc structure at 35 kbar and Yb at 40 kbar. Both are good metals after

the transition. With such striking parallels it seems natural to attempt to explain the behavior of both metals by the same mechanism. Clearly any mechanism which explains the Yb transition on the basis of the promotion of a 4f electron to a conduction band is entirely inappropriate for Sr. Strontium has no electrons which could conceivably be promoted to a conduction band.

The explanation of the resistance behavior evidently appears to lie in the premise that the first and second bands are unlapping with pressure. This leads to the semiconducting behavior. The first two bands are strongly overlapped after the phase transition, resulting in metallic conduction. The phase transition may take place just because the new phase allows for a lowering of the average energy of the conduction electrons because of the overlap of the first two conduction bands.

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FIGURE CAPTIONS

Fig. 1. Angular correlation curve for Yb at 9.7 kbar.

Fig. 2. Effect of pressure on the Fermi momentum of ytterbium.

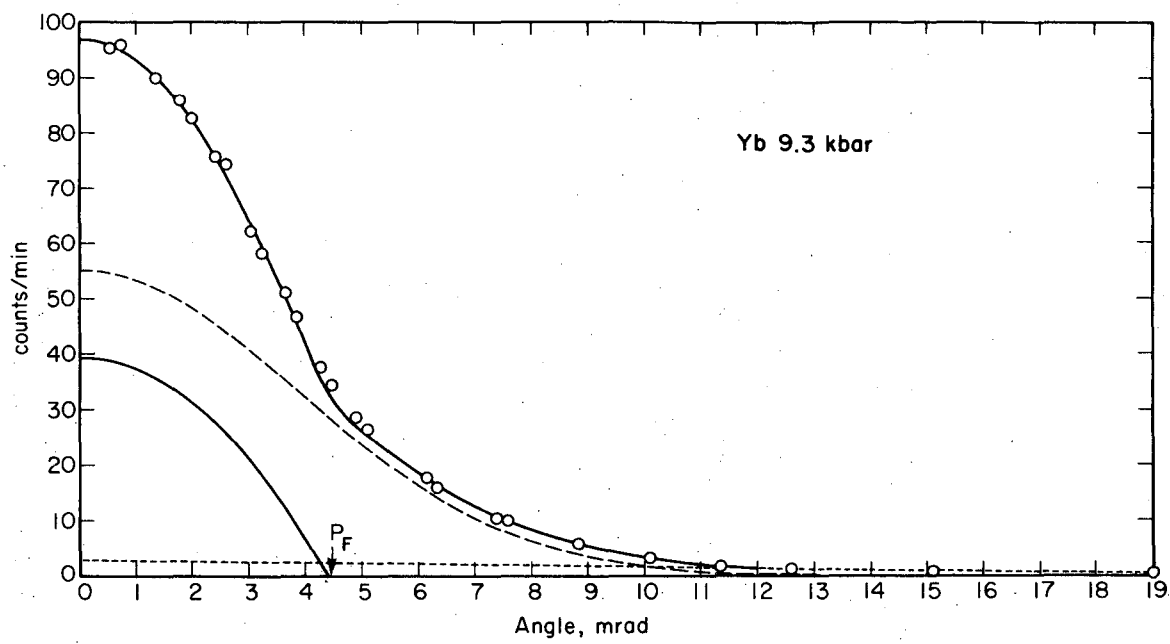
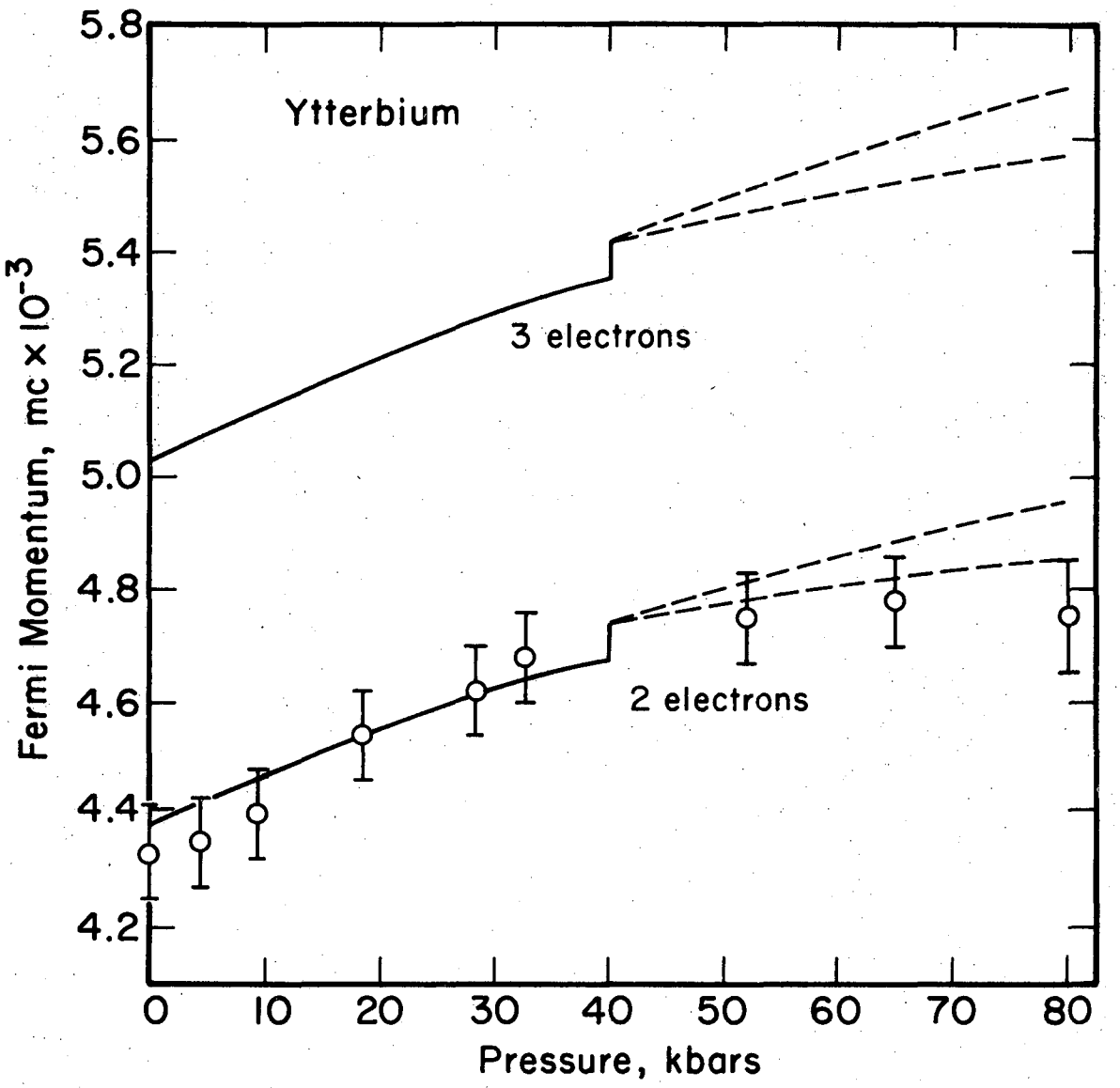

Yb 9.3 kbar
counts/min
Angle, mrad
P_F
0
10
20
30
40
50
60
70
80
90
100
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
XBL 711-6437

Fig. 1.



XBL 711-6438

Fig. 2.

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