Robins reports a weak peak at 15 eV in the electron energy loss experiment for Cd which he identifies as the volume plasma loss. Our data show no enhanced emission at this energy. Likewise, the 17.0-eV peak in Robins' data for Zn was not observed in the present work. Robins found intense losses at 7.5 eV in Cd and at 8.6 eV in Zn which he identifies as surface plasmon losses. The emissions observed by us at 9.1 eV in Cd and at around 8.6 eV in Zn must be due either to transitions from the valence band to holes in inner shells or to volume plasma oscillations. Either interpretation would lead to the conclusion that the identification of these losses by Robins as surface plasmons is incorrect. The fact that these losses are the strongest and sharpest in these elements also leads one to doubt their identification as surface plasmons. Further experiments of this type should help to clarify the nature of these characteristic losses.

PHYSICAL REVIEW VOLUME 137, NUMBER 5A 1 MARCH 1965

Search for Superconductivity in α-Cerium

T. F. Smith*
University of California, San Diego, La Jolla, California

(Received 28 September 1964)

The α modification of cerium, formed from the normal, room-temperature modification under a pressure of 10 000 atm, has been cooled to 1.25°K and tested for superconductivity. The nature of the state of the $4f$ electron in α-cerium is discussed in relation to the absence of superconductivity.

INTRODUCTION

It is well-known that the normal, room temperature, face-centered cubic γ cerium transforms to the denser α-cerium at around 110°K, retaining the face-centered cubic structure.[1,2] The transformation is due to a change in the electronic configuration, the single $4f$ electron of α-cerium going into the conduction band. This transformation can be induced at room temperature by the application of high pressure (≈ 8000 atm).[3–6]

It is doubtful whether the bound, or virtually bound state character associated with the f electron is completely removed in the transformation since various investigators have proposed values for the number of conduction electrons ranging from 3.5 to 4.0 for α-cerium. The evidence for the number of conduction electrons of α-cerium has been reviewed by Gschneidner and Smoluchowski.[7]

Should the bound-state character of the cerium be removed, one might expect that it would be very similar electronically, with the addition of a conduction electron, to the face-centered cubic modification of its superconducting neighbor lanthanum. Due to this similarity, one might expect that α-cerium would also exhibit superconducting properties.

Unfortunately, from the point of view of investigating the possible superconducting properties of α-cerium, a further modification of cerium forms at 250°K. Hexagonal β-cerium is considered to have the same number of conduction electrons as γ-cerium, the f electron retaining its bound state character.[7] As the temperature is reduced further, γ-cerium transforms to α-cerium. At low temperatures, therefore, the specimen consists of a mixture of α- and β-cerium. The exact proportions of the two forms depend on the thermal history.[8–10] In view of the disastrous effect of rare-earth additions on the superconducting transition temperature of lanthanum,[11] the presence of β-cerium would inhibit the possible superconducting properties of α-cerium prepared by cooling γ-cerium. It was therefore proposed to subject the γ-cerium to a sufficiently high pressure at room temperature, transforming it directly to the α phase. The α-cerium would then be cooled, without removing it from the pressure capsule, by immersion in a bath of liquid helium IV.

APPARATUS

The pressure capsule was modeled on that of Bowen and Jones[12] and was constructed throughout of Be-Cu.

---

* Research supported in part by the U. S. Air Force Office of Scientific Research.

[1] A. W. Lawson and T. Tang, Phys. Rev. **76**, 301 (1949).

[2] A. F. Schuch and J. H. Sturdivant, J. Chem. Phys. **18**, 145 (1950).

[3] P. W. Bridgman, *The Physics of High Pressures* (G. Bell and Sons Ltd., London, 1952).

[4] A. I. Likher, Yu. N. Ryabinin, and L. F. Vereshchagin, Zh. Eksperim. i Teor. Fiz. **33**, 610 (1957) [English transl.: Soviet Phys.—JETP **6**, 469 (1958)].

[5] R. Herman and C. A. Swenson, J. Chem. Phys. **29**, 398 (1958).

[6] E. G. Ponyatovski, Doklady Akad. Nauk SSSR **120**, 1021 (1958) [English transl.: Soviet Phys.—Doklady **3**, 498 (1958)].

[7] K. A. Gschneidner, Jr., and R. Smoluchowski, J. Less-Common Metals **5**, 374 (1963).

[8] C. J. McHargne, H. L. Yakel, Jr., and L. K. Jelter, Acta Cryst. **10**, 832 (1957).

[9] C. J. McHargne and H. L. Yakel, Jr., Acta Met. **8**, 637 (1960).

[10] K. A. Gschneidner, Jr., R. O. Elliott, and R. R. McDonnald, Phys. Chem. Solids **23**, 1191 (1962).

[11] B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Letters **1**, 92 (1958).

[12] D. H. Bowen and G. O. Jones, Proc. Roy. Soc. (London) **A254**, 522 (1960).

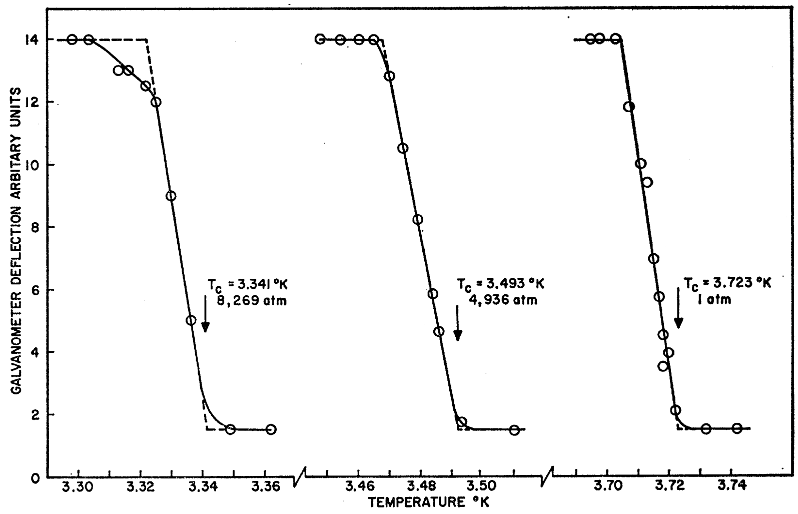

FIG. 1. Typical superconducting transition curves for tin. The pressures marked on the curves have been calculated from ΔT_c.

The compressive force on the sample was applied through a piston from a laboratory press capable of delivering 24 000 lbs. wt. Disks of Teflon packing were placed above and below the sample to prevent extrusion of the sample between the piston and the cylinder wall, which would cause pressure gradients and consequently broadening of superconducting transitions. The sample was retained in a state of compression by means of a clamp, which was screwed down on the piston when the desired pressure was achieved. The entire assembly could then be removed from the press. The occurrence of superconductivity was detected ballistically by means of coils mounted around the specimen space. The temperature of the sample was varied between 1.2 and 4.2°K by pumping on the bath of liquid helium IV in which the pressure capsule was immersed. Temperatures in this range were measured from the vapor pressure over the helium bath, using the 1958 temperature scale. In the event of temperature measurements above 4.2°K a calibrated carbon resistor was embedded in the base of the pressure capsule.

SAMPLES

The cerium used in this investigation was obtained from the Research Chemicals Corporation and was stated to have a 99.9% purity. The manufacturers spectrographic analysis report gave the following impurities: La 0.03, Nd 0.02, Pr 0.03, Ta 0.09, Si 0.01, Mg 0.01, and Ca 0.03 in wt %. Fe, Ni, and Co were not detected within the limits of the analysis. Samples were made from two separate batches. The cylindrical samples were cut to approximately the correct size to fit into the pressure capsule. These were then compressed in the capsule to the exact dimensions. The samples were then sealed in evacuated quartz tubes and annealed at 500°C for several hours and then water quenched to ensure that the entire sample was in the γ phase. The samples were retained in the sealed tubes, to prevent oxidation, until just before they were required. Very slight surface discoloration was removed with abrasive paper just before placing the samples in the pressure capsule.

A sample of polycrystalline tin, purity 99.99% supplied by Johnson Matthey, was used in the pressure calibration of the capsule.

MEASUREMENTS

Pressures calculated from the scale reading in pounds on the press and the area of the piston were compared with values determined from the known pressure variation of the superconducting transition temperature T_c of tin. No corrections to the calculated values were made for friction, distension of the cylinder bore, or the effects of relative thermal expansion on cooling the capsule. Such corrections were to be taken into account in the calibration with the tin. The transition temperature of the tin at 1 atm was determined in the pressure capsule to ensure identical conditions for all the superconductivity measurements. The superconducting transition temperature was taken as the high-temperature extrapolation of the linear portion of the transition curve. Typical measured transition curves are shown in Fig. 1. The uniformity of the applied pressure is indicated in the sharpness of the transitions. The transition temperature determined after releasing the pressure showed no significant difference from the initial value.

Pressures were calculated from ΔT_c using the empirical relationship $\Delta T_c = -4.95\times10^{-5}P + 3.9\times10^{-10}P^2$ determined by Jennings and Swenson.[13] Pressures calculated in this manner are compared, in Table I, with those determined from the piston dimensions and the reading on the press. As expected, pressures calculated from the scale readings are consistently greater than

---

[13] L. D. Jennings and C. A. Swenson, Phys. Rev. **112**, 31 (1958).

TABLE I. The variation of the superconducting transition temperature T_c of tin with applied pressure. P_{obs} is pressure calculated directly from capsule dimension; P_{cal} is pressure determined from ΔT_c using the empirical relationship of Jennings and Swenson (Ref. 13).

T_c(°K)	ΔT_c(°K)	P_{obs}(atm)	P_{cal}(atm)
3.732	...	...	...
3.493	0.230	5050	4940
3.400	0.323	7010	6900
3.361	0.362	8240	7800
3.341	0.382	9100	8270
3.288	0.435	10 580	9380

those calculated from ΔT_c. The maximum difference occurs at the higher pressures and is approximately 10% of the pressure calculated from the scale reading. Pressures calculated directly from the scale reading, with the appropriate correction applied, are considered accurate to within 5%.

In the present investigation, however, an exact knowledge of the pressure on the cerium wasu nnecessary, it being sufficient to know that the γ-α transformation pressure had been exceeded. To ensure this, the displacement of the piston was observed for various scale readings on the press. A discontinuity in the displacement, which was in very good agreement with the known volume change[3] of approximately 15% at the γ-α transition, occurred between 13 500 and 15 000 lbs. This corresponds to a pressure range of approximately 7500 to 9000 atm for the transition, a value in reasonable agreement with previous investigations.[4–6]

Three independent temperature runs were made down to 1.25°K, using two samples and a maximum pressure of approximately 10 000 atm. No trace of superconductivity was observed down to this temperature.

CONCLUSION

The failure to detect superconductivity in α-cerium may, of course, be due to an inherent lack of such a property. Alternatively, from a consideration of the occurrence of superconductivity in the early transition elements, it is tempting to speculate on the possibility of superconducting α-cerium. Sc and Y in Group III.B, with three conduction electrons, have not as yet been found to be superconducting, whereas the elements of Groups IV.B and V.B, with four and five conduction electrons, respectively, are all superconducting. As the elements of Group V.B have consistently higher transition temperatures it would seem that one could associate the increase in transition temperature with the increase in the number of conduction electrons. One might suppose, therefore, that α-cerium, having one more conduction electron than lanthanum, would be superconducting with a higher transition temperature.

If we first adopt the view of Lounasmaa[14] and Wilkinson *et al.*[15] that there is no localized magnetic moment in α-cerium, we may argue that although there is no bound or virtual bound state of the $4f$ electron in α-cerium, some $4f$ character remains. It is this $4f$ character, admixed with d, p, and s character, in the wavefunctions for the conduction electrons which then inhibits the occurrence of superconductivity. However, as there is undoubtedly $4f$ character in the wavefunction for the conduction electrons of lanthanum, this does not seem likely. One might even speculate that it is the presence of the $4f$ character in lanthanum which accounts for the occurrence of superconductivity absent in Sc and Y.

A more probable explanation for the absence of superconductivity is that the maximum pressure used in the present investigation was insufficient to remove completely the bound state character of the $4f$ electron in α-cerium. Extending the search to higher pressures may resolve this situation.

ACKNOWLEDGMENTS

The author is indebted to Dr. W. E. Gardner for a number of informative discussions and his comments on this manuscript. Thanks are due to Professor J. L. Olsen for his advice on high-pressure measurements, and Mr. B. Maple for his assistance in the construction of the apparatus.

---

[14] O. V. Lounasmaa, Phys. Rev. **133**, A502 (1964).

[15] M. K. Wilkinson, H. R. Child, C. J. McHargne, W. C. Koehler, and E. O. Wollan, Phys. Rev. **122**, 1409 (1961).