similar correlation has been observed by Pierce and Blann for lighter projectiles.[5]

There is not enough evidence to say whether this correlation is more than a useful fortuitous fact since the concept of an effective charge for an energetic ion in a solid is vague at best. If the electronic stopping power does follow the dependence of the mean charge of ions in gases, then differences, similar to the differences in the mean charges between I and U ions in air reported by Betz *et al.*[16] (see Fig. 5), should be observable in the electronic slowing down process. Unfortunately, the present data do not cover a large enough range of reduced velocities to be sensitive to such deviations. More accurate data, taken over a wider range of energies of very heavy ions are needed in order to detect any possible dependence of the stopping process on the mass of the projectile.

It is worth remarking that if the effective charge deduced from dE/dX measurements is indeed a physically meaningful quantity, then, perhaps, the potential charge experienced by the ions on their passage from the solid into vacuum may cause the stripping of some extra, weakly bound, electrons thus leaving the ions emerging from the solid in a higher-charge state than they had inside the solid.[5] The present data show that in such a model as many as 14 electrons may be lost by 140-MeV Ta ions when emerging from a foil. There is no evidence for or against such a "stripping" effect though it is perhaps more likely that in solid media extra screening accounts for the closeness of the effective charge in solids and gases.

ACKNOWLEDGMENTS

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Positron Annihilation in γ- and α-Cerium*

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The $\gamma\rightarrow\alpha$ phase transition of cerium has been investigated by measurement of the positron lifetime and angular correlation of positron-annihilation radiation in the two phases. The lifetime in the α phase was observed to be 8% shorter than the lifetime in the γ phase when the α phase was produced by the application of pressure; and it was observed to be 5% longer when the α phase was produced by lowering the temperature. The angular correlation from α-cerium produced by pressure was observed to be slightly broader than that from γ-cerium, in contrast to the narrowing previously observed when α-cerium was produced by lowering the temperature. Since the observed changes are much smaller than predicted by models which explain the $\gamma\rightarrow\alpha$ transition by assuming a transfer, or partial transfer, of the $4f$ electron to the conduction band, it is concluded that such electronic promotion does not occur.

INTRODUCTION

The $\gamma\rightarrow\alpha$ transition of cerium metal is of interest because it involves a change in lattice size without a change in structure. Both phases are fcc. The normal γ phase has a lattice constant of about 5.16 Å, while the collapsed α phase has a lattice constant of about 4.85 Å, depending on the temperature and pressure. The transformation from the γ phase to the α phase can be induced either by lowering the temperature below 100°K or by applying a pressure of about 8 kbar. Since the single $4f$ electron of cerium extends farther from the center of the atom than the $4f$ electrons of the other lanthanide elements and is close, energetically, to the conduction electrons, it is doubtlessly involved in the $\gamma\rightarrow\alpha$ transition. Zachariasen[1] and Pauling[2] independently proposed that the transformation was due to the transfer of the $4f$ electron to the valence band. More recently, Gschneidner and Smoluchowski[3] proposed that the transfer is only partial. They arrived at a valence of about 3.6 for α-cerium, the exact value depending upon the temperature and pressure, from calculations using the metallic radius and the magnetic susceptibility.

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* Work supported in part by the National Science Foundation.

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

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

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

While a wide variety of experiments[4-11] has shown that there is a change of electronic structure upon transformation, there has been no direct confirmation of the proposed electronic promotion. However, most of these experiments have shown that the $4f$ electron is involved in the transformation. A method which is capable of examining the valency is the positron-annihilation method. Both the lifetime of positrons and the angular correlation of positron-annihilation radiation are sensitive to the valence of the metal in which they annihilate. Such investigations should therefore be a reliable test of the $4f$ promotion model.

The first investigation of the lifetime of positrons in the lanthanide metals was made by Rodda and Stewart.[12] They found that the variation of the lifetime with the valence was in agreement with the predictions of Kahana.[13] As expected, they found that the lifetime in γ-cerium was consistent with a valence of 3. They did not investigate the lifetime in α-cerium. Measurements of the angular correlation of annihilation radiation made by Gustafson and Mackintosh[14] showed that the angular correlation also was sensitive to the valence of the lanthanide metals. Their measurement on γ-cerium was consistent with a valence of 3 also. However, when they subsequently measured the angular correlation at 4.2°K,[15] where the sample would be approximately half α-cerium,[4] they found that the change in the angular correlation was in the direction opposite to that predicted by the $4f$ promotion model.

The present work extends the study of positron annihilation in cerium by measuring the lifetime as a function of temperature and as a function of pressure and by measuring the angular correlation as a function of pressure. The present results cannot be explained using the $4f$ promotion model.

EXPERIMENTAL PROCEDURES

The lifetimes were measured using conventional multichannel delayed-coincidence methods supplemented by pulse-height compensation. The γ-ray detectors consisted of Naton 136 plastic scintillators coupled to 56AVP photomultipliers. The instrumental resolution was 0.59 nsec during the temperature measurements and 0.54 nsec during the pressure measurements. The resolution was taken as the full width at half-maximum of a cobalt-60 time spectrum measured with the energy selection discriminators set at energies appropriate to a sodium-22 positron source.

The angular correlations were measured using the standard parallel-slit geometry. The slits were 16×0.065 in. and were located 10 ft from the sample, thus defining an angular resolution of 0.54 mrad. The time resolution of the fast-coincidence circuit was 10 nsec, which was sufficiently fast to reduce the chance-coincidence rate to an insignificant level. This was essential because an internal positron source was used.

The cerium used for the measurement of lifetime as a function of temperature was obtained from the American Potash and Chemical Corp. and had a stated purity of 99.9% with respect to other rare earths. The cerium used for the measurement of lifetime and angular correlation as a function of pressure was obtained from the Cerac Corp. and was 99.9% pure. The samples used in both phases of the pressure work were cut from the same cerium ingot. The cerium was cut into pieces of the appropriate size and vacuum annealed in a tantalum crucible at 700°K for more than two days before being allowed to vacuum cool to room temperature. Since the hexagonal β phase transforms into the γ phase at 440°K,[8] the samples were in the γ phase after annealing. The annealing also reduced the number of vacancies present which could alter both the lifetimes[16] and the angular correlations.[17] The samples were prepared by sandwiching a positron source between two pieces of cerium, the surfaces of which were cleaned with a fine grade of abrasive paper. The sample used for the measurement of lifetime as a function of temperature was kept in either helium gas or a vacuum at all times to prevent oxidation of the cerium. During the pressure measurements, the sample assembly was subjected to a pressure of 1 kbar immediately after assembly to prevent oxidation of the cerium. The positron sources used for the lifetime measurements were prepared by depositing sodium-22 in HCl solution on a small piece of 0.2-mil-thick Mylar and then evaporating the liquid. A second piece of Mylar was cemented to the first, thereby completely enclosing the radioactive material. Approximately 8 μCi of sodium-22 were used for the temperature measurement while about 35 μCi were used for the measurement of lifetime as a function of pressure. The pressure measurement required a more intense source because the small ports of the high-pressure cell necessitated the use of smaller scintillators. The positron source used for the angular correlation measurements consisted of 25 mCi of cobalt-58 plated on and diffused into a 0.25-mil copper foil.

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

[5] J. M. Lock, Proc. Phys. Soc. (London) **B70**, 566 (1957).

[6] A. I. Likhter and V. A. Venttsel, Fiz. Tverd. Tela **4**, 485 (1962) [English transl.: Soviet Phys.—Solid State **4**, 352 (1962)].

[7] C. R. Burr and S. Ehara, Phys. Rev. **149**, 551 (1966).

[8] K. A. Gschneidner, Jr., R. O. Elliott, and R. R. McDonald, J. Phys. Chem. Solids **23**, 555 (1962).

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

[10] K. A. Gschneidner, Jr., R. O. Elliott, and R. R. McDonald, J. Phys. Chem. Solids **23**, 1201 (1962).

[11] B. L. Davis and L. H. Adams, J. Phys. Chem. Solids **25**, 379 (1964).

[12] J. L. Rodda and M. G. Stewart, Phys. Rev. **131**, 255 (1963).

[13] S. Kahana, Phys. Rev. **129**, 1622 (1963).

[14] D. R. Gustafson and A. R. Mackintosh, J. Phys. Chem. Solids **25**, 389 (1964).

[15] D. R. Gustafson and A. R. Mackintosh, Bull. Am. Phys. Soc. **10**, 376 (1965).

[16] B. T. A. McKee, H. M. B. Bird, and I. K. MacKenzie, Bull. Am. Phys. Soc. **12**, 687 (1967).

[17] S. Berko and J. C. Erskine, Phys. Rev. Letters **19**, 307 (1967).

The low-temperature lifetime measurements were made by placing the sample in a cylindrical brass vessel, 1 in. diam and 3 in. long, which was positioned inside the Dewar and in contact with the cryogenic fluid. The vessel was attached to a thin stainless-steel tube which allowed it to be evacuated or filled with helium gas. The sample assembly was held by a brass spring in a slot machined in the upper end of a copper pedestal designed to position the sample centrally within the vessel and to provide thermal contact between the sample and the vessel. During changes in temperature, the chamber was filled with helium gas to increase the thermal coupling between the sample and the chamber. During measurements, it was evacuated. The lifetime was measured at 300, 77, and 4.2°K. In order to minimize the formation of β-cerium, the temperature was lowered to 77°K as quickly as possible by direct quenching of the sample chamber in liquid nitrogen. At no time during the cooling from 300 to 4.2°K was the temperature of the sample allowed to increase.

The pressure measurements were made in an opposed piston cell with 0.25-in.-diam steel pistons and 0.38-in. beryllium alloy walls. The cell, shown in Fig. 1 was patterned after the cell used by Davis and Adams[11] for an x-ray diffraction investigation of the $\gamma \rightarrow \alpha$ transition. The angular correlations were measured through the two diametrically opposed ports, while the lifetimes were measured using two ports located 90° apart. The pressure was calculated from the measurement of the pressure of the hydraulic fluid and the size of the cell and hydraulic ram. Sample extrusion and resultant internal friction appeared to be slight. Consequently, the pressure uncertainty was almost entirely due to the error of the pressure gauge. The pressure uncertainty was estimated to be less than ±2 kbar at 20 kbar.

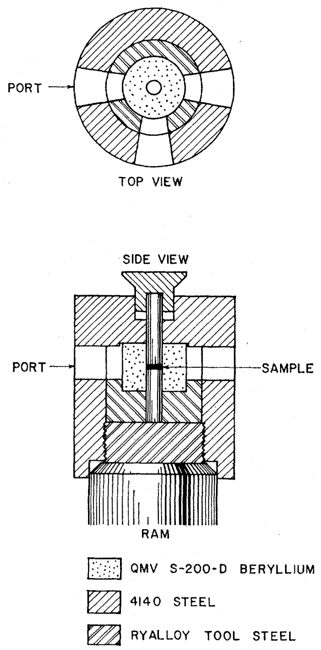

FIG. 1. Beryllium-walled high-pressure cell used for the measurement of the variation of lifetime and angular correlation with pressure. The cell is shown with the cap removed to show the ports in the top view.

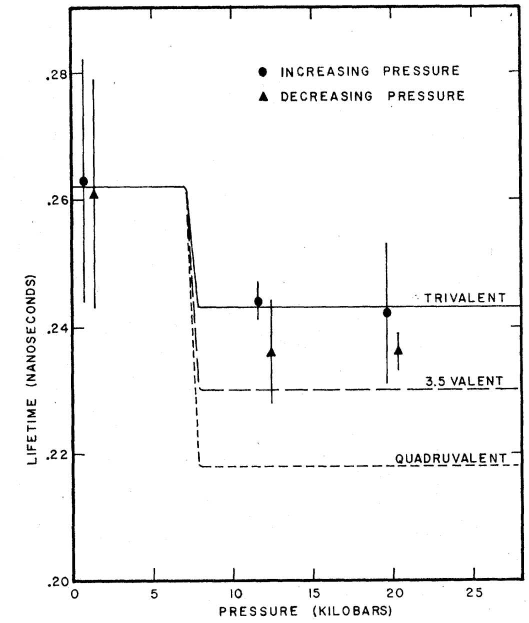

FIG. 2. Positron lifetime in cerium as a function of pressure. The points are the measured values, while the curves are the lifetimes calculated using Kahana's predictions (Ref. 18) assuming valences of 3, 3.5, and 4 for α-cerium. The calculated value was normalized to the measured value at 1 kbar.

RESULTS

The lifetime was measured as a function of pressure at nominal pressures of 1, 12, and 20 kbar on the first compression cycle after annealing and at pressures of 20, 12, and 1 kbar on the subsequent decompression cycle. The lifetimes, derived from an analysis of the centroid shift of the time spectra, are shown in Fig. 2. The lifetime at 1 kbar was the same before and after the compression cycle. Figure 3 shows the lifetime measured as a function of temperature, at temperatures of 300, 77, and 4.2°K, on the first cooling cycle after annealing.

Although the agreement between the low pressure, 300°K lifetimes measured in the low-temperature system and the high-pressure system was not good, both measurements are in agreement with the lifetime in γ-cerium (0.244±0.013 nsec) found by Rodda and Stewart.[12] The discrepancy was probably due to the different counter geometries used in the two experimental setups. The scintillators for the temperature measurement were about 1 in. in diameter, while the scintillators used during the pressure measurement were only 0.3 in. diam in order to fit into the ports of the

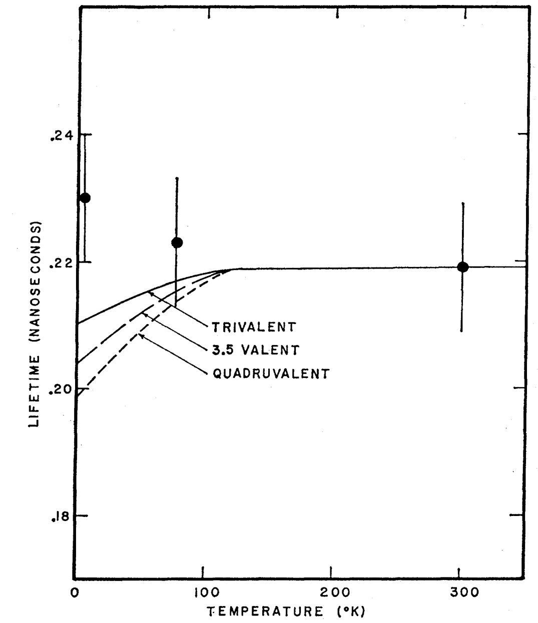

FIG. 3. Positron lifetime in cerium as a function of temperature. The points are the measured values, while the curves are the lifetimes calculated using Kahana's predictions (Ref. 18) assuming valences of 3, 3.5, and 4 for α-cerium and 50% conversion into α-cerium at 4.2°K. The calculated lifetime was normalized to the measured lifetime at 300°K.

high-pressure cell. The differences in source strength, in the amount of scattering, and in attenuation of the annihilation radiation in the two different geometries also may have contributed to the difference. There is, therefore, some question as to which value is the more reliable; however, there is no reason to believe that the relative variation during either phase of the work is in error. Since the relative variation is far more relevant to the question of the valency of α-cerium than the absolute lifetime, the difference in the two absolute lifetimes is not of major importance.

The angular correlations are shown in Fig. 4 for pressure values of 1, 12, and 20 kbar. For clarity, smooth curves were drawn through the individual data points. The measurements were made on the first compression cycle after annealing; however, the angular correlation at 1 kbar was remeasured after the 20-kbar measurement, and it was identical to the original 1-kbar angular correlation. The 1-kbar angular correlation is nearly the same as the angular correlation in γ-cerium at 300°K measured by Gustafson and Mackintosh,[15] shown for comparison in Fig. 5. The small difference at large angles was due to the use of an internal positron source in the present experiment.

DISCUSSION

The lifetime and angular correlation are determined by both the positron and electron wave functions. However, in a metal the role of the positron is secondary to that of the electron, since the positron is in a very low momentum state and its spatial distribution is fairly slowly varying. It is possible that the change in the positron wave function accompanying the $\gamma \rightarrow \alpha$ contraction could cause minor changes in the annihilation characteristics; however, it would be very difficult to construct an explanation of the present results based on the premiss that the expected changes in the annihilation characteristics due to an increase in the valence are compensated for by changes in the positron wave function. The reason is that such an explanation would require the positron wave function to become strongly peaked in a region which simultaneously has a low electron density and low average momentum. There is no likely mechanism to induce such a drastic behavior in the positron wave function. Thus in the following discussion the behavior of the positron will be assumed to cause only minor changes in the annihilation characteristics.

The change in lifetime that would be expected when γ-cerium transforms into α-cerium can be calculated from the lattice parameters of the two phases and the variation in lifetime with electron density predicted by Kahana.[13,18] Although Kahana did not include the effect of the lattice potential upon the conduction electrons in his computations, the application of his predictions to cerium can be justified by the close agreement between the calculated and measured variation of lifetime as a function of valency in the rare-earth metals.[12] The calculated lifetimes, assuming valences of 3, 3.5, and 4 for α-cerium, are shown in Figs. 2 and 3. In each figure the calculated lifetimes were normalized to the experimental lifetimes at 1 kbar and 300°K for the γ phase. The transformation is assumed to be complete for the pressure-induced transformation, while in the temperature-induced

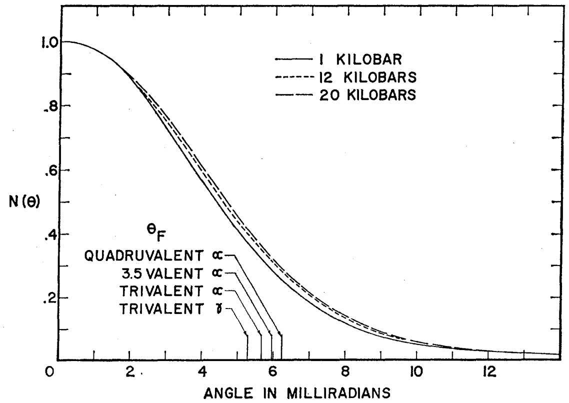

FIG. 4. Angular correlation in cerium measured as a function of pressure. θ_F was calculated from the free-electron theory assuming valences of 3 for γ-cerium and 3, 3.5, and 4 for α-cerium.

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[18] S. Kahana, in *Proceedings of the Wayne State University Positron Annihilation Conference, Detroit, 1965*, edited by A. T. Stewart and L. O. Roellig (Academic Press Inc., New York, 1967), p. 51.

transformation the amount of the α phase was assumed to be the same as that observed by Wilkinson *et al.*[4] for a sample with a similar history; specifically, 10% at 77°K and 50% at 4.2°K.

When the $\gamma \rightarrow \alpha$ transformation was induced by lowering the temperature, the positron lifetime was found to increase, which is in contrast to the decrease expected for an assumed α-cerium valence of 3 or greater. This anomalous increase is in agreement, however, with the low-temperature angular correlation measurements of Gustafson and Mackintosh[15] shown in Fig. 5. They found a decrease in the width of the angular correlation upon lowering the temperature while an assumed valence of 3 or greater for α-cerium would predict an increase in the width. If these changes are attributed only to the portion of the sample which was in the α phase, then the increase in lifetime and the narrowing of the angular correlation in α-cerium alone would be approximately twice as large as the observed changes, because only about half the sample was α-cerium. There are two likely causes for the observed behavior. Either of these or a combination of both would explain the results: The first is that the electronic structure of α-cerium at low temperatures may be considerably different from the electronic structure of α-cerium at high pressure and room temperature, even though the lattice constant is essentially the same. There is considerable evidence suggesting that this is the case. For example, the transition is observed to have a critical point at about 700°K and 20 kbar.[11,19–21] This implies that the electronic structure of one or both phases must change as a function of temperature and pressure. The experimental evidence indicates that it is the α phase which undergoes the larger variation. Gschneidner and Smoluchowski[3] also cite numerous reasons why the electronic structure of α-cerium is probably not the same under both sets of conditions, although their conclusions on the exact nature of the difference are not consistent with the present observations. The second possible cause is the creation of vacancies when the transformation occurs. McKee *et al.*[16] showed that some metals show an increase in lifetime of up to 30% when subjected to severe deformation, presumably due to the creation of vacancies. Berko and Erskine[17] noted a narrowing of the angular correlation in aluminum when it was deformed, also presumably due to vacancy creation. Thus, if one assumes that vacancies are the cause of the observed increases in lifetime, it is difficult to draw any conclusions about the valence state of α-cerium from the lifetime measurements. However, it is doubtful that the number of vacancies created by cooling an annealed cerium sample was as large as the number created by McKee *et al.* when they intentionally severely deformed the sample, and it would be difficult to explain the narrowing of the angular correlation with decreasing temperature solely on the basis of vacancies. Even if it is assumed that the angular correlation in α-cerium at low temperatures is narrowed by the same amount as observed in severely deformed aluminum, the measured angular correlation in 50% α-cerium would not be consistent with an assumed valency greater than 3 for α-cerium. Thus it can be concluded from the results of positron annihilation that the valence of α-cerium at low temperatures is not significantly greater than 3. In addition, the positron-annihilation results indicate that the electronic structure of α-cerium may be dependent on the temperature and pressure.

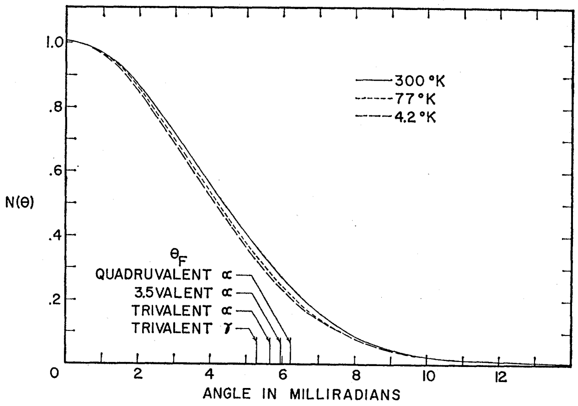

FIG. 5. Angular correlation in cerium measured as a function of temperature. θ_F was calculated from the free-electron theory assuming a valence of 3 for γ-cerium and 3, 3.5, and 4 for α-cerium (from Ref. 15).

The variation of lifetime with pressure is also consistent with an assumed valence for α-cerium of 3, although a valence of 3.5 cannot be ruled out (see Fig. 2). An assumed valence of 4 predicts a variation in lifetime which is much larger than observed. Recently, MacKenzie and LeBlanc[22] have investigated the lifetime in the alkali metals as a function of pressure and found that the decrease in lifetime caused by the increase in the electron density with pressure was considerably larger than that calculated by Kahana.[13,18] Since it is not yet clear whether all metals would show similar behavior, this effect may or may not be important in cerium. It should be pointed out, however, that if this effect is important in cerium, the calculated lifetime change would be greater than shown and the agreement with a valence of 3 would be improved. The effect of vacancies in α-cerium created by the application of pressure at 300°K would not be expected to be large because it is unlikely that a significant number were formed. This view is confirmed by the apparent

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[19] E. Poniatovskii, Dokl. Akad. Nauk SSSR **120**, 1021 (1958) [English transl.: Soviet Phys.—Doklady **3**, 498 (1958)].

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

[21] R. I. Beecroft and C. A. Swenson, J. Phys. Chem. Solids **15**, 234 (1960).

[22] I. K. MacKenzie and R. LeBlanc, Bull. Am. Phys. Soc. **12**, 1039 (1967).

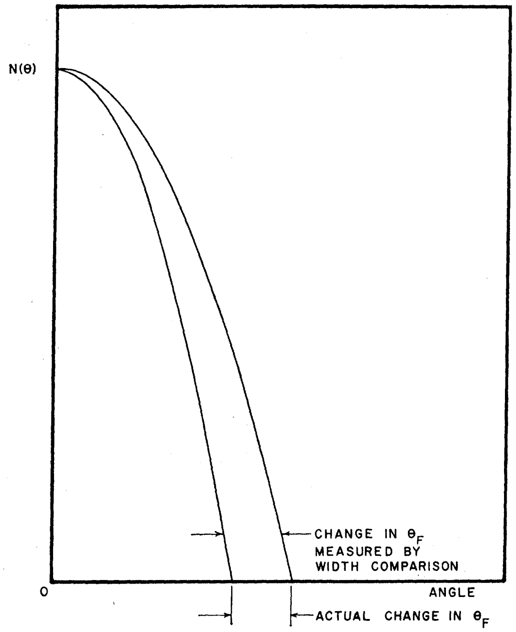

FIG. 6. Two representative free-electron angular correlations illustrating the measurement of the change of the Fermi-surface radius by measurement of the difference in the width of the angular correlations.

absence of hysteresis in both the lifetime and the angular correlation when pressure was released returning the cerium to the γ phase.

The accuracy of the angular correlation method for the determination of the valence of a metal is dependent on the electronic structure of the metal. If the metal is free-electron-like with a nearly spherical Fermi surface, the angular correlation will be close to parabolic and will have a sharp change in slope at θ_F, the angle corresponding to the Fermi-surface radius. In such a metal the valence determination is accurate to within a few percent. On the other hand, if the Fermi surface is highly distorted, the valence cannot be found by angular-correlation measurements. The fcc phases of cerium have an electronic structure which is between these two extremes; the free-electron model provides a useful first approximation but does not predict the detailed behavior of cerium. This is evident in the observed angular correlations: While there is no sharp change in slope at θ_F for cerium, the shape of the angular correlations is basically parabolic at low angles and, by comparison with divalent ytterbium, one can assign a valence of approximately 3 to normal γ-cerium,[14] in agreement with the lifetime measurements.[12] The determination of the change in valence by measurement of the change in the angular correlation can be justified by a consideration of how it could be applied to a free-electron metal. Suppose one had angular correlations from two free-electron metals (or phases) which had similar values for θ_F, such as shown in Fig. 6. Assume the two parabolic curves are normalized to have equal height at zero angle. In this example, one could determine the change in the Fermi-surface radius either by locating the changes in slope at θ_F, or if the slope changes were obscured for some reason, one could measure the difference in width of the two curves in the angular region near θ_F. In the case of cerium, the latter method is applicable because the change in width is essentially the same for a wide range of angles near θ_F. The free-electron model predicts the following increases in width: 0.34±0.03 mrad if α-cerium is trivalent, 0.65±0.03 mrad if α-cerium has a valence of 3.5, and 1.03±0.03 mrad if α-cerium is quadruvalent. The uncertainties are due to the uncertainties in the lattice constants. The measured increase in the width when the pressure is increased from 1 kbar (γ-cerium) to 20 kbar (α-cerium) in the region near θ_F is 0.30±0.03 mrad. This is in agreement with the change predicted if α-cerium remains trivalent and far smaller than predicted for a change in valence from 3 to 3.5 or 4. Consequently, it is not possible to explain the present results within the framework of the $4f$ promotional model, and it is concluded therefore that the promotional model is not correct.

Even though the promotional model does not provide an adequate explanation of experiment, there is little doubt that the $4f$ electron plays an important role in the transition. If the $4f$ electron does not leave the $4f$ state, the alternative must be that the $4f$ state changes. One possibility is that it changes from a highly localized state which acts as a virtual scattering state[23] in γ-cerium into a $4f$ band in α-cerium. When the properties of the system as a whole are considered, this transition would be continuous[24,25] and would not produce a significant change in the angular correlation or positron lifetime. Although this transition from a localized state to a $4f$ band would have little effect on the results of positron annihilation, such properties as conductivity, magnetic susceptibility, and the Hall effect would be altered. Since the overlap of the $4f$ electrons is greater in cerium than in the other lanthanide metals, the decrease in atomic spacing when γ-cerium is transformed to α-cerium may result in the conversion of the localized $4f$ level into a $4f$ electron band. Another possible explanation of the $\gamma \rightarrow \alpha$ transition is spin compensation of the $4f$ magnetic moment by the conduction electrons, as suggested by Coqblin and Blandin.[26] Edelstein[27] has extended this suggestion to show that spin compensation provides a satisfactory explanation of the observed magnetic properties of cerium and is also consistent with the present results.

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[23] A. Blandin, B. Coqblin, and J. Friedel, in *Physics of Solids at High Pressure*, edited by C. T. Tomizuka and R. M. Emrich (Academic Press Inc., New York, 1965), p. 233.

[24] W. Kohn and C. Majumdar, Phys. Rev. **138**, A1617 (1965).

[25] C. Majumdar, J. Math. Phys. **7**, 682 (1966).

[26] B. Coqblin and A. Blandin, Advan. Phys. **17**, 281 (1968).

[27] A. S. Edelstein, Phys. Rev. Letters **20**, 1348 (1968).