

## Coexistence of Intermediate Valence and Antiferromagnetic Ordering in Europium Metal

J. N. Farrell<sup>(a)</sup> and R. D. Taylor

*Physics Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

(Received 25 November 1986)

Mossbauer-effect measurements show that for Eu metal, intermediate-valence and antiferromagnetic-ordering states coexist over the pressure range 0 to 14 GPa for temperatures below the Néel temperature of about 90 K. As the average valence increases with pressure up to 12 GPa, the magnetization decreases because of a dilution of the average magnetic moment per atom.

PACS numbers: 75.30.Mb, 62.50.+p, 71.70.Ch, 76.80.+y

Two of the striking properties found in certain rare-earth solids are intermediate valence and magnetic ordering. Both properties are related to a spatial and energetic localization of the  $f$  electrons. Both arise in appropriate cases as a result of changes in pressure, temperature, or chemical composition. Despite the similarities in their origins, the two properties have appeared to be incompatible in most kinds of rare-earth systems in which either has been seen.

Intermediate valence is a phenomenon whereby two different  $f$ -electron states for an atom in a solid lie close enough in energy that neither is strongly favored over the other. Instead, the configuration fluctuates between integral  $f$ -shell occupations. The average  $f$ -shell and therefore valence-electron occupation can have a value intermediate between integral values.<sup>1</sup>

Rare-earth atoms can have configurations with  $4f$ -shell magnetic moments, giving rise in many cases to magnetic ordering phenomena. Little is known in detail about the pressure dependence of rare-earth magnetism as a result of the difficulty of making magnetic measurements in a high-pressure cell.

Still less is known about the relationship between intermediate valence and magnetism. It is in intermediate-valence systems involving a mixture of magnetic and nonmagnetic  $f$ -electron states (i.e., with Ce, Sm, Eu, or Yb, but not Tm) that a seeming incompatibility between the two phenomena is seen. Several recent experimental<sup>2-4</sup> and theoretical<sup>5,6</sup> studies have addressed the possibility of a coexistence of intermediate valence and magnetic ordering in such systems.

Europium systems provide examples of both phenomena. From the point of view of localized  $f$  moments in Eu, the intermediate-valence state involves a mixture of magnetic ( $4f^7$ ) and nonmagnetic ( $4f^6$ ) states. One might wonder to what extent magnetic ordering can survive a change in average occupation towards the nonmagnetic state. Empirically, a coexistence of the two phenomena has never been unambiguously observed in Eu systems. Eu solids in which intermediate valence has been seen have not shown magnetic ordering, and Eu solids with magnetic ordering have not shown intermediate valence.

Eu metal, the subject of the present study, exhibits both phenomena of interest. Eu metal is antiferromagnetic at low temperature and ambient pressure.<sup>7</sup> At high pressure and room temperature Eu has a continuous valence transition.<sup>8,9</sup> We show that below the Néel temperature (90 K at 1 atm) the same kind of valence transition takes place, though magnetic ordering is still present. We find that increasing pressure causes the magnetization to decrease as the valence changes towards a state with a smaller average magnetic moment. The decrease in magnetization takes place proportionally faster than the valence change.

The measurements were carried out by <sup>151</sup>Eu Mössbauer spectroscopy on samples contained in a diamond anvil cell. This kind of spectroscopy affords a means of simultaneously measuring information pertaining to both the  $f$ -electron occupation and the degree of magnetic ordering in Eu systems.

The two key quantities determined from the Mössbauer measurements are the isomer shift and the magnetic hyperfine field. Both quantities are measured at the nuclear sites, the former giving information about the  $f$ -shell occupation and the latter about magnetism of the solid. Since the lifetime of the nuclear transition for a Mössbauer  $\gamma$  ray is much longer than the charge-fluctuation time in an intermediate-valence system, what we measure is a spectrum showing the effect of an average magnetic field and average  $f$ -electron occupation. Figure 1 shows how the splitting of the <sup>151</sup>Eu  $\gamma$ -ray resonance pattern changes with pressure as a result of changes in magnetic field, while the centroid of the pattern moves in accordance with changes in the  $f$ -shell occupation.

The method we have used for the data analysis does not take into account the saturation of the Mössbauer resonance absorption due to the absorber thickness. For less-resolved hyperfine field patterns, it becomes increasingly difficult to distinguish between the magnetic and thickness effects. Thus with our present counting statistics and data-analysis method we cannot determine magnetic critical temperatures precisely.

Pressures were applied with a Merrill-Basset-type diamond cell with 1-mm-diam tips. The  $\approx 50\text{-}\mu\text{m}$ -thick

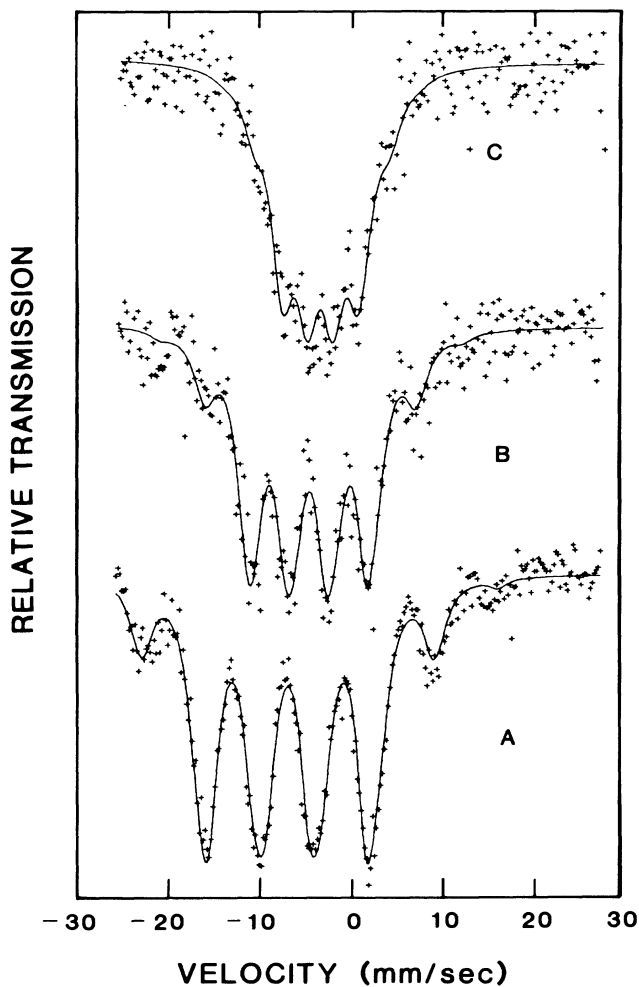


FIG. 1. Mössbauer spectra of Eu metal at 44 K and 0, 6.2, and 9.8 GPa applied pressure. The single-line  $\text{SmF}_3$  source is at 44 K.

sample was placed in a 300- $\mu\text{m}$  hole in a gasket prepressed to an 80- $\mu\text{m}$  thickness. A liquid-argon pressure-transmitting medium was used instead of the usual alcohol mixture because of the highly reactive nature of Eu. The gasket used was made of 90% Ta-10% W alloy, a high-atomic-weight material which helped to collimate the 22-keV Eu gamma rays. Pressures were measured with the ruby fluorescence method.

A 150-mCi, 4-mm active diameter,  $^{151}\text{SmF}_3$  source was used. Counting rates were rather low in this work, only 5 to 20 per second. Nonetheless, as a result of the great sensitivity of the  $^{151}\text{Eu}$  Mössbauer effect, a spectrum could be accumulated in one or two days.

We have made systematic Mössbauer measurements at pressures ranging from 0 to 14 GPa at  $44 \pm 1$  K. This temperature, which was chosen for experimental convenience, is well below the Néel temperature found previously as a function of pressure from resistivity measurements.<sup>9</sup> The results are depicted in Figs. 2-4.

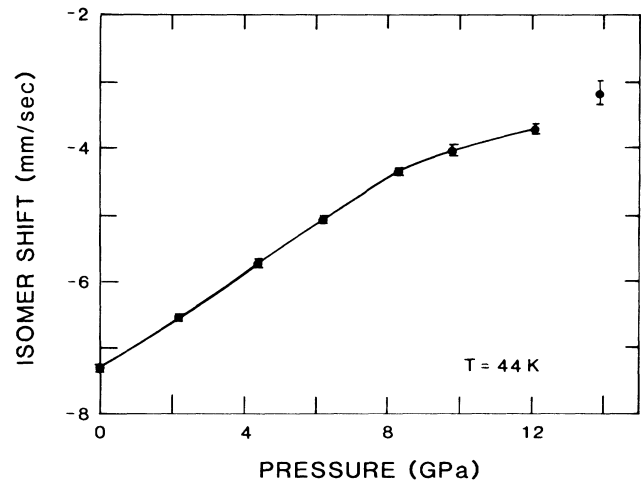


FIG. 2. Mössbauer isomer shift of  $^{151}\text{Eu}$  in metal vs  $^{151}\text{SmF}_3$  as a function of pressure. Source and absorber are at the same temperature.

The Mössbauer isomer shift changed from  $-7.3$  to  $-3.7$  mm/s over this range of pressure (Fig. 2). The exact correspondence of the isomer shift to the  $f$ -shell occupation for  $^{151}\text{Eu}$  depends on the particular solid system involved, and is not precisely known for Eu metal. Using a linear interpolation, we estimate a change of  $\approx 0.4$  electron, a considerable valence change. This change is the same as was found at room temperature with Mössbauer measurements.<sup>10</sup> Röhler has recently made a measurement of the average valence of Eu metal at room temperature and high pressure by use of the  $L_{III}$  x-ray edge absorption method.<sup>11</sup> In that work a change of  $\approx 0.45$  electron over the same pressure range was found.

The magnitude of the hyperfine magnetic field at 44 K changes from 22 to 8 T over the pressure range 0-12

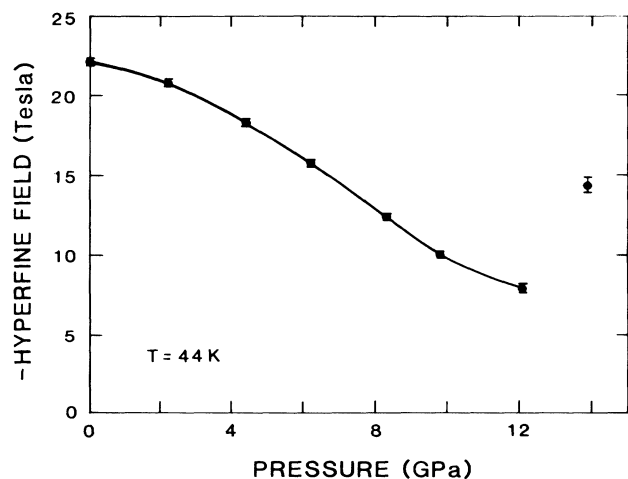


FIG. 3. Pressure dependence of the magnetic hyperfine field at the nucleus for  $^{151}\text{Eu}$  in Eu metal.

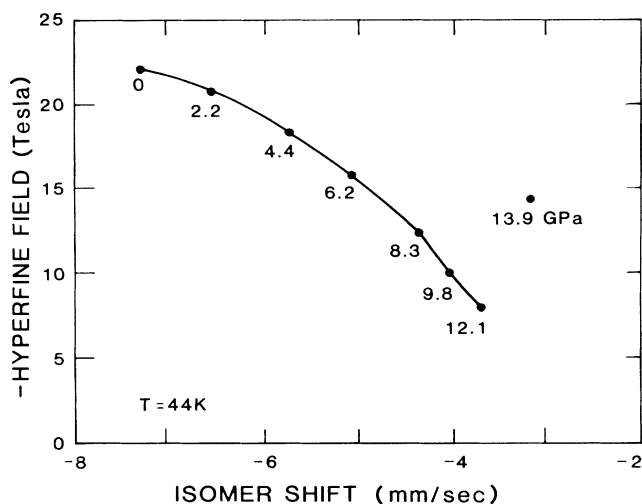


FIG. 4. Comparison of the isomer shift and magnetic hyperfine field for Eu metal at 44 K and high pressure. Pressures are marked along the curve.

GPa (Fig. 3). This decline is due mostly to a dilution of the average magnetic moment of the Eu atoms as a result of the valence change, not a decrease in  $T_N$ . Thus the spontaneous magnetization in the solid survives over the entire valence transition range studied.

At 13.9 GPa and 44 K the Mössbauer spectrum is more complex and seems to be shifted towards higher valence. A preliminary examination of the data suggests a magnetic character with additional quadrupolar or phase-mixing effects. An increase in temperature to 75 K narrows the line pattern, which at 90 K appears to be a single line. We have fitted the pattern at 44 K with a single magnetic Eu site and find that the magnetic field at 13.9 GPa and at 44 K is *larger* than at 12.1 GPa. Most likely Eu transforms between 12.1 and 13.9 GPa into a new phase, perhaps the hexagonal phase seen at such pressures at room temperature.<sup>8</sup>

Figure 4 shows the relationship between the isomer shift and the magnetic hyperfine field. The smooth curve expressing this relationship for the low-pressure phase extrapolates to an isomer shift of about  $-3$  mm/s for zero hyperfine field, a shift corresponding to a valence change of about 0.5 electron. This value might give an indication of the coexistence range possible for bcc Eu metal had the structural phase transition not taken place near 13 GPa.

We also have made measurements at some other temperatures. Measurements at 4 K and pressures of 4.4 and 12 GPa show approximately the same amount of valence change as at 44 and 293 K, and the same kind of decline in magnetic ordering with pressure as at 44 K. At a pressure 9.8 GPa and temperatures of 44, 59, and 75 K, the magnetic field decreases. At 9.8 GPa the Néel temperature appears to be near 75 K.

The kind of measurement we are performing allows the determination of a pressure-temperature phase diagram for the valence, magnetic, and, to a lesser extent, structural properties of Eu systems. Our preliminary results confirm the results of Bundy and Dunn<sup>9</sup> for the pressure dependence of the Néel temperature up to 12 GPa in Eu. In addition, we show that there is a change in the magnetic and probably structural properties of Eu at around 13 GPa and below about 90 K. The results in Ref. 9 suggest the existence of three distinct phases in temperature at pressures in excess of 20 GPa. We plan to carry out Mössbauer measurements in these regions.

The isomer shift and thus the valence change in Eu metal are strongly dependent on pressure but not on temperature. In contrast, for intermetallic Eu compounds with large valence changes there is a dependence on both temperature and pressure.<sup>3</sup> Perhaps this implies a very large characteristic valence-fluctuation temperature for Eu metal.

The great decrease in the size of the Eu unit cells under pressure (40% at 12 GPa) might tend to strengthen the exchange field in the solid. Indeed, an *increase* in the magnitude of the hyperfine magnetic field at the nucleus with pressure is most often the case in other Eu systems.<sup>12,13</sup> The pressure dependence of magnetism in Eu metal likely involves competing mechanisms.

Room-temperature measurements for Eu reveal a saturation of the valence change at pressures above 14 GPa.<sup>10,11</sup> Later we hope to see whether the magnetization increases or decreases with increasing pressure in the saturation region. Also, in other systems such as EuO and EuS known to have intermediate valence,<sup>10,14</sup> the magnetic hyperfine field increases with pressure for pressures below the onset of the valence transition.<sup>12</sup> Perhaps a reversal of the pressure dependence of the hyperfine field in those systems can be observed when the valence change occurs.

A pressure-induced collapse of magnetic ordering occurring along with a valence change was reported previously<sup>3</sup> for the intermetallic compound  $\text{Eu}(\text{Pd}_{0.8}\text{Au}_{0.2})_2\text{Si}_2$ . The Mössbauer effect was used to show drastic valence and magnetic changes at 4 K and below 1.2 GPa. A valence range was determined over which intermediate valence and magnetic ordering should coexist. However, an unambiguous coexistence for the two phenomena could not be demonstrated in that material because of the narrow range of the valence transition with pressure as well as the multiplicity of inequivalent Eu sites, each with differing valence transition properties. In Eu metal, we clearly observe a coexistence. On the other hand, in the present work we do not observe the complete destruction of magnetic ordering with pressure. The mechanism suggested for the collapse of magnetic ordering in  $\text{Eu}(\text{Pd}_{0.8}\text{Au}_{0.2})_2\text{Si}_2$  was a crossing of the highly pressure-dependent Néel transition.

As mentioned above, the intermediate valence and magnetic ordering phenomena appear to be incompatible

for other Eu systems. In the case of Eu metal, while we can see a clear coexistence of the two phenomena, the question remains of whether an incompatibility instead is manifested as a kind of competition. It is shown in this work that the degree of magnetic ordering present depends on the degree of valence change produced (as well as the usual temperature dependence). The opposite dependence, that of the valence change on magnetism, has not been demonstrated. Thus we do not show a competitive relationship between the two properties. Similar studies carried out with an applied magnetic field might show such a competition.

We have shown in this work that in Eu metal at high pressure and below the Néel temperature, the intermediate valence and magnetic ordering phenomena coexist. The magnetization of Eu is strongly dependent on the valence and temperature, while the valence is insensitive to changes in the magnetization and temperature. Extended systematic pressure-temperature measurements of these properties and relationships are underway. These and similar measurements should provide unique insights into the difficult theoretical problem of magnetic and electronic interactions in rare-earth solids.

We wish to thank D. Wohlleben for valuable suggestions, and J. Mullen for helpful assistance pertaining to this work. This work was supported by the U.S. Depart-

ment of Energy.

---

(a)Present address: Teledyne Brown Engineering, Huntsville, AL 35807.

<sup>1</sup>R. D. Parks, *Hyperfine Interact.* **24-26**, 565 (1985).

<sup>2</sup>C. V. Segre, M. Croft, J. A. Hodges, V. Murgai, L. C. Gupta, and R. D. Parks, *Phys. Rev. Lett.* **49**, 1947 (1982).

<sup>3</sup>M. M. Abd-Elmeguid, Ch. Sauer, and W. Zinn, *Phys. Rev. Lett.* **55**, 2467 (1985).

<sup>4</sup>H. G. Zimmer, K. Takemura, K. Syassen, and K. Fischer, *Phys. Rev. B* **29**, 2350 (1984).

<sup>5</sup>B. H. Brandow, *Phys. Rev. B* **33**, 215 (1986).

<sup>6</sup>W. Nolting and A. Ramakanth, *Phys. Rev. B* **33**, 1838 (1986).

<sup>7</sup>K. A. McEwen, in *Handbook of the Physics and Chemistry of the Rare Earths*, edited by K. A. Gschneidner and L. R. Eyring (North-Holland, Amsterdam, 1978), Vol. 1, p. 433.

<sup>8</sup>K. Takemura and K. Syassen, *J. Phys. F* **15**, 543 (1985).

<sup>9</sup>F. P. Bundy and K. J. Dunn, *Phys. Rev. B* **24**, 4136 (1981).

<sup>10</sup>J. N. Farrell and R. D. Taylor, *Bull. Am. Phys. Soc.* **31**, 500 (1986).

<sup>11</sup>J. Röhler, to be published.

<sup>12</sup>U. F. Klein, G. Wortmann, and G. M. Kalvius, *J. Magn. Magn. Mater.* **3**, 50 (1976).

<sup>13</sup>M. M. Abd-Elmeguid, H. Micklitz, and G. Kaindl, *Phys. Rev. B* **23**, 75 (1981).

<sup>14</sup>K. Syassen, *J. Phys. (Paris)*, *Colloq.* **45**, C8-123 (1984).