

the interaction term reach more than a small fraction of its potential value which could, in principle, double the infinite separation value of the total scattering power of a pair of identical defects. Thus, the linearity up to surprisingly high concentrations of the resistivity of dilute alloys is explained in terms of the insensitivity of total scattering cross section to defect separation. Further, the theory permits the prediction that, provided that the total lattice relax-

ation associated with the defect pair is not greatly modified in the process, the joining of two lattice vacancies into a divacancy will not result in a large fractional change in residual resistance.

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Ferromagnetism in $\text{EuH}_2^{\dagger\dagger}$

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Magnetic measurements have been made on a Eu-H sample of composition represented by the formula $\text{EuH}_{1.86}$ over a temperature range extending from 4.2° to 300°K. The magnetization-temperature data for the sample, which for simplicity is termed EuH_2 , indicate a Curie point at 24°K. Field dependency studies in the liquid helium range reveal saturation effects and remanence, confirming that EuH_2 has become ferromagnetic at these temperatures. The observed saturation moment at 4.2°K is $\sim 6.0\mu_B$ (Bohr magnetons) per Eu atom. For $T > 30^\circ\text{K}$ the susceptibility shows a Curie-Weiss dependence on temperature and the effective moment is $8.4\mu_B$ per Eu atom. EuH_2 , the saturated hydride of Eu, is unlike the highest (i.e., saturated) hydrides of the other lanthanide metals which have been studied— GdH_3 , TbH_3 and HoH_3 —in that it alone exhibits magnetic ordering at low temperatures. As the hydrogen-saturated metals lack conduction electrons, the coupling between the localized $4f$ electrons is expected to be very weak and magnetic ordering is expected to occur only at very low temperatures if at all. Thus the behavior of the several trihydrides is in keeping with expectation whereas that of EuH_2 is not. The coupling mechanism in this case is not well understood; it may be due to direct overlap of the $4f$ orbitals.

STUDIES of lanthanide hydrides show that when they are hydrogenated to saturation, they cease to be metallic conductors.¹⁻³ This and other properties⁴ of these materials indicate that when hydrogen is taken into the metal, it absorbs electrons from the conduction band to form the H^- anion and, moreover, in the fully hydrogenated metal the conduction band is entirely depopulated. Acquisition of the supernumerary hydrogen electron from the conduction band rather than from the core electrons is confirmed by the fact that the magneton number is unaffected by hydrogenation.

The removal of the conduction electrons in the lanthanide metals should have strong implications as regards the cooperative magnetic phenomena which occur in these materials at low temperatures, since exchange in them is generally regarded as operating via the conduction electrons. Specifically, we might expect

that alignment in the hydrides will, if it occurs at all, develop at temperatures much lower than in the corresponding element. This expectation has been confirmed for the fully hydrogenated materials HoH_3 ,⁵ TbH_3 and GdH_3 ,⁶ which give no indication of either Curie or Néel points down to 4.2°K. In addition, for HoH_2 and TbH_2 , in which the conduction band is considerably depleted, the Néel points are quite low compared to the parent metal, occurring at 8° and 45°K, respectively.⁶ After observing these gratifyingly predictable behaviors, we decided to examine the hydride of the more complex metal europium. Among the lanthanides Eu is atypical in that (1) its structure is bcc, (2) it is divalent and hence at saturation forms only a dihydride, and (3) the question of whether its moments are aligned at low temperatures (i.e., $<10^\circ$ to 15°K) is regarded by some as being as yet unsettled.⁷

Europium was hydrogenated using techniques previously employed in this laboratory.⁴ Despite very considerable effort the maximum hydrogen content

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^{††} This work was assisted by a contract with the U. S. Atomic Energy Commission.

¹ B. Stalinski, *Bull. acad. polon. sci.* **5**, 1001 (1957) and **7**, 269 (1959).

² J. C. Warf and K. Hardcastle, Office of Naval Research, Final Report August, 1961, (unpublished).

³ T. Peltz and W. E. Wallace, (unpublished measurements).

⁴ A. Pebler and W. E. Wallace, *J. Phys. Chem.* **66**, 148 (1962).

⁵ Y. Kubota and W. E. Wallace, paper presented at the Seventh Annual Conference on Magnetism, November, 1961 and submitted to *J. Appl. Phys.*

⁶ Y. Kubota, R. L. Zanowick, and W. E. Wallace (to be published).

⁷ See, for example, R. M. Bozorth, and J. H. Van Vleck, *Phys. Rev.* **118**, 1493 (1960).

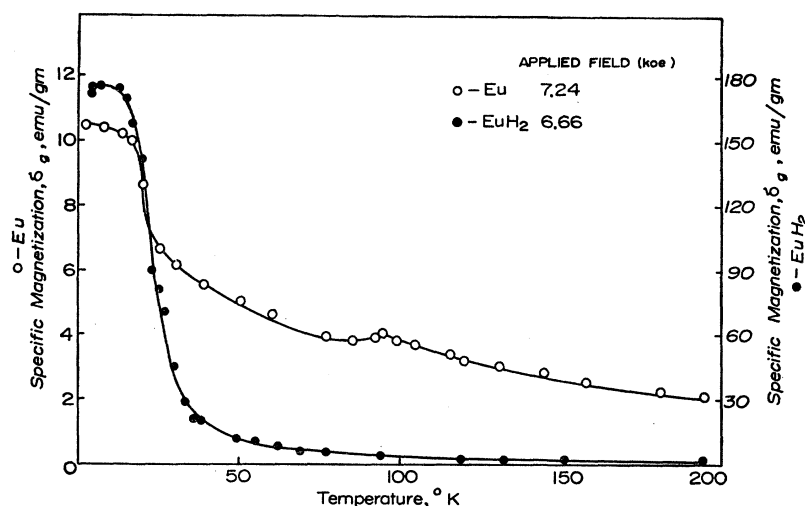


FIG. 1. Magnetization-temperature curves for EuH_2 and Eu .

attainable was that corresponding to the formula $\text{EuH}_{1.86}$. The hydride forms as a fine powder which oxidizes rapidly in air. Hence, no diffraction information on it was obtained, and we were not certain whether the Eu was all present in the hydride phase or the sample contained $\text{EuH}_2 + 7\%$ metallic Eu . From visual inspection and the magnetic results, however, we believe it to have been the former. The magnetic measurements were made on the $\text{EuH}_{1.86}$ sample, which for simplicity we call EuH_2 .

Europium dihydride gives every indication that it is ferromagnetic at low temperatures. Its magnetization-temperature behavior (Fig. 1) suggests a Curie point at about 25°K . Furthermore, measurements of σ vs H at 4.2°K (Fig. 2) exhibit tendencies to saturate and noticeable hysteresis even at rather low fields. Taking these as overt evidences of ferromagnetism the Curie temperature at 6.7 koe is established to be 24°K from a σ^2 vs T

plot. The saturation moment was obtained from a σ vs $1/H$ plot and was found to be $\sim 6\mu_B$ per Eu atom. This value is only approximate since the highest field currently available⁸ in this laboratory when the magnet gap is widened to accommodate the helium cryostat is 7.5 koe and some curvature is still apparent in the σ vs $1/H$ plot at the maximum fields employed.

We wish in each case to intercompare the magnetic behavior of the hydride with that of the corresponding element. Accordingly, to enhance the reliability of this comparison we always examine the lanthanide along with the hydride. The results obtained for elemental Eu plotted in Fig. 1 show a maximum at about 95°K , in agreement with the measurements of Bozorth and Van Vleck.⁷ These observations suggest that antiferromagnetic ordering occurs at this temperature and this has recently been confirmed by neutron diffraction work.⁹ Above the Néel point we note for Eu , again in agreement with the results of Bozorth and Van Vleck, a linear dependence of inverse susceptibility with temperature. They reported an effective moment of $8.3\mu_B$ per Eu atom which corresponds closely with the value $8.4\mu_B$ found in the present work.

In contrast with the element the σ - T plot for EuH_2 gives no indication of a Néel point. Evidently in this case the material becomes ferromagnetic on cooling without having first traversed an antiferromagnetic region. Its susceptibility for temperatures above about 30°K is given quite precisely by the expression $\chi = 6.62/(T - 25)$, which leads to a magneton number of $7.0\mu_B$ per Eu atom.

These results indicate a different situation when EuH_2 is compared with Eu than that which is revealed when the Ho , Tb or Gd hydrides are compared with their

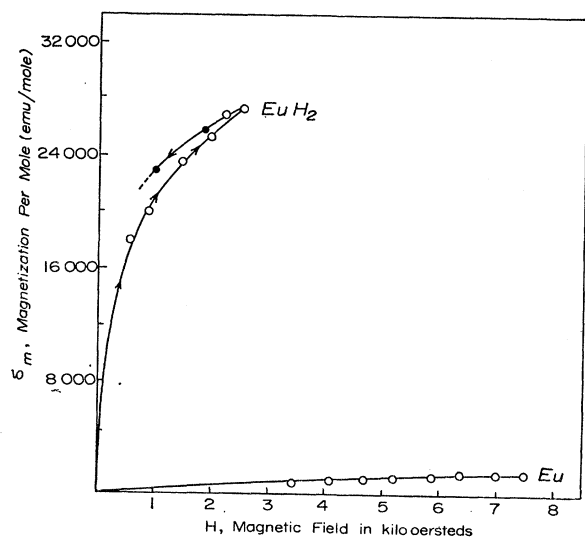


FIG. 2. Magnetization curves at 4.2°K for EuH_2 and Eu .

⁸ Equipment is under construction which will permit measurements to ~ 25 koe.

⁹ C. E. Olsen, N. G. Nereson, and G. P. Arnold, paper presented at the Seventh Annual Conference on Magnetism, November, 1961 (unpublished).

parent metals. As was pointed out above, hydrogenation of these metals suppressed entirely the tendency to order ferromagnetically in every instance. Only for the dihydrides is there evidence of alignment, and it is antiferromagnetic in nature. Between 30 and 90°K europium orders, so that its moments are in a flat spiral.⁹ Its magnetic structure at low temperatures is as yet unknown but the observed magnetization behavior suggests the existence of some new type of antiferromagnetic structure below 25°K—a conical arrangement, another kind of spiral, or perhaps a complex ferrimagnetic alignment of the moments. Thus, in this case hydrogenation destroys both antiferromagnetic structures and leads to what appears to be a classical ferromagnet (and one which is relatively soft magnetically) in the case of the hydride.

The present results suggest that the conduction electrons are essential to the special interactions which produce the antiferromagnetic structures in Eu. It

should be noted, however, that hydrogenation of Eu produces a change in crystallographic structure which puts the Eu^{++} 's into an approximately cph arrangement.¹⁰ Hence, it is not clear whether the absence of antiferromagnetism in the hydride is due to the lack of conduction electrons or to its different mode of packing.

In view of the localized nature of the 4*f* electrons it is not clear how the ferromagnetic exchange interactions occur in EuH_2 , which is presumably an insulator. The recent discovery of ferromagnetism in EuO by Matthias *et al.*¹¹ raises a similar question. In this connection we note that not only is the structure in EuH_2 less open than in Eu but the Eu-Eu distance is smaller by 0.2 Å in the hydride than in the metal. The metal contracts considerably upon hydrogenation, perhaps to the extent that appreciable direct exchange in this case occurs.

¹⁰ W. L. Korst and J. C. Warf, *Acta Cryst.* **9**, 452 (1956).

¹¹ B. T. Matthias, R. M. Bozorth, and J. H. Van Vleck, *Phys. Rev. Letters* **7**, 160 (1961).