

On the basis of our experiments, we cannot interpret the results with the model of the random flipping of the hyperfine field.<sup>1</sup> (The sidebands observed at 4 Mc/sec could not possibly be detected in supermalloy samples, as in Perlow's experiment, because of the large width of the Mössbauer lines at  $H_{rf}=0$ .) Furthermore, the calculation of  $x^2$  given above for the case of iron has been carried out also for supermalloy samples. The relatively smaller values of  $k^2$  for the latter can be compensated by the relatively larger magnetic energy density. Consequently, the model of the magnetostriction might be valid for supermalloy, if it is for iron.

In conclusion, the present experiments yield the following information:

(a) The sidebands observed in iron slabs of various thicknesses in the presence of a rf magnetic field cannot be described by a single "modulation index"; a quantum-mechanical derivation of their spectrum accounts satisfactorily for the obtained results.

(b) The dependence of the intensity of the sidebands on the static magnetic field  $H_0$ , perpendicular to  $H_{rf}$ , suggests that the domain-wall contribution, if any, to the observed effect is much smaller than the contribution of the rotation of domain magnetization.

(c) The magnetostriction model accounts for the intensity of the sidebands, if the magneto-elastic coupling coefficient  $k^2$  is assumed to be much larger in the dynamic condition than in the static condition.

## First-Order Phase Transition in Europium Metal

R. L. COHEN, S. HÜFNER,\* AND K. W. WEST

*Bell Telephone Laboratories, Murray Hill, New Jersey 07974*

(Received 24 March 1969)

We have used Mössbauer-effect measurements of the hyperfine (hf) interaction in Eu metal to study the behavior of its sublattice magnetization in the vicinity of the magnetic ordering temperature. At 88.6°K, the hf field falls from 0.4 of the saturation value to zero. This results from the existence of a first-order transition coincident with the magnetic ordering. The possible causes of the transition are discussed. The temperature dependence of the hyperfine field just below the transition is analyzed in terms of critical-point theory. The results of thermal-expansion measurements are also presented and discussed.

### I. INTRODUCTION

THERE has been a renewed interest in the behavior of substances in the vicinity of critical points of their phase diagrams<sup>1</sup> ever since the derivation of the "scaling laws." In particular, many investigations of magnetic systems in the vicinity of the ordering temperature have been performed, though there are a number of difficulties connected with the extraction of the relevant parameters from the experimental data. In particular, the temperature dependence of the sublattice magnetization has been measured for a number of compounds in the vicinity of the critical temperature. With this aim in mind, a measurement of the temperature dependence of the hyperfine (hf) fields in Eu metal was undertaken.<sup>2</sup> As a result of these measurements, we found that the paramagnetic to antiferromagnetic transition in Eu metal is of first order. This article mainly presents the experimental

evidence of this and discusses the causes for the first-order transition, and only secondarily will we discuss the result in terms of a critical-point analysis. For clarity, we have chosen to call the temperature at which the hf field disappears  $T_t$  ( $=88.6\pm 0.3^\circ\text{K}$ ) in our sample. The term  $T_N$  represents the temperature at which the hf field, extrapolated on the basis of a power law from points just below  $T_t$ , would go to zero if the first-order transition did not take place.  $T_N$  is about 1°K above  $T_t$ .

In addition to the Mössbauer measurements, a thermal-expansion measurement was performed in order to check whether there was any anomalous change of the lattice parameters at the magnetic ordering temperature.

There are two previous measurements on the Mössbauer effect in Eu metal.<sup>3,4</sup> These experiments did not observe the sharp transition reported here, probably because of inadequate sample purity.

### II. PROPERTIES OF Eu METAL

Eu is divalent in Eu metal, which has bcc structure. This can be inferred from the isomer shift observed in

\* Present address: Freie Universität Berlin, Berlin, West Germany.

<sup>1</sup> Recent work has been surveyed in two extensive reviews: L. P. Kadanoff *et al.*, *Rev. Mod. Phys.* **39**, 395 (1967); P. Heller, *Rept. Prog. Phys.* **30**, 731 (1967).

<sup>2</sup> Preliminary results were reported in S. Hüfner, R. L. Cohen, and K. W. West, *Bull. Am. Phys. Soc.* **13**, 876 (1968). The present measurements were performed on samples of greater purity than the rolled metal foils used earlier.

<sup>3</sup> P. H. Barrett and D. A. Shirley, *Phys. Rev.* **131**, 123 (1963).

<sup>4</sup> P. Kienle, *Rev. Mod. Phys.* **36**, 372 (1963).

Mössbauer measurements, specific heat,<sup>5</sup> magnetization,<sup>6,7</sup> and neutron diffraction<sup>8</sup> measurements as well as from the different atomic volume as compared to the neighboring rare-earth metals in the periodic table. It should be particularly stressed that the Mössbauer measurements give no indication that even a small fraction of the Eu ions is in a trivalent state. Therefore, the Eu ions have a  $^8S_{7/2}$  ground state. The first excited state of the  $4f^7$  configuration is  $^6P_{7/2}$  at about  $25\,000\text{ cm}^{-1}$ , and, therefore, it lies far above the ground state. The magnetic structure of Eu has been determined from neutron diffraction<sup>8</sup> experiments as being "flat spiral." The Eu-ion moments, with a value of  $(5.9 \pm 0.4)\mu_B$ , lie in layers in the cube faces (all the moments in one face plane being parallel) with a turn angle of about  $50^\circ$  between the moments in adjacent layers; this turn angle is constant from  $T=0^\circ\text{K}$  up to about  $T=0.8T_i$  and then increases slightly to  $53^\circ$  close to  $T_i$ . The temperature of the magnetic transition has been found to lie near  $90^\circ\text{K}$ .<sup>3-6,8</sup> Additionally, magnetization measurements<sup>7</sup> have revealed a large magnetic anisotropy because in fields as high as 140 kOe, saturation could not be obtained. The exchange has been shown recently to be of relatively long range.<sup>9</sup> Band-structure calculations<sup>10</sup> have shown that the  $d$  bands lie very near to the Fermi surface and, therefore, the electronic properties of Eu metal should reflect the  $d$  character of the conduction bands.

The hf field  $H$  in Eu comes primarily from core polarization due to the  $4f$  electrons and from conduction electron polarization.<sup>9</sup> Since both these terms are proportional to sublattice magnetization,  $H$  should also be. However, because the magnetic spiral angle changes with temperature, the contribution of the conduction electron polarization to the hf field is not exactly proportional to the  $4f$  moment. This effect is unimportant in this work.

### III. MÖSSBAUER-EFFECT MEASUREMENTS

#### A. Experimental Technique

The hf interaction was studied using the Mössbauer effect in transmission geometry with a standard constant-acceleration spectrometer.<sup>11</sup> The source was  $\text{Sm}_2\text{O}_3$  containing  $\text{Sm}^{151}$ , which undergoes  $\beta$  decay to the 21.7-keV state in  $\text{Eu}^{151}$ . The source was held at about  $78^\circ\text{K}$  during the experiments. All isomer shifts quoted are relative to an absorber of  $\text{Eu}_2\text{O}_3$  at  $78^\circ\text{K}$ .

<sup>5</sup> B. C. Gerstein, F. J. Jelinek, J. R. Mullaly, W. D. Schickell, and F. H. Spedding, *J. Chem. Phys.* **47**, 5194 (1967).

<sup>6</sup> R. M. Bozorth and J. H. Van Vleck, *Phys. Rev.* **118**, 1493 (1960).

<sup>7</sup> M. Schieber, S. Foner, R. Dolco, and E. J. McNiff, Jr., *J. Appl. Phys.* **39**, 885 (1968).

<sup>8</sup> N. G. Nereson, C. E. Olsen, and G. P. Arnold, *Phys. Rev.* **135**, A176 (1964).

<sup>9</sup> S. Hüfner and J. H. Wernick, *Phys. Rev.* **173**, 448 (1968).

<sup>10</sup> O. K. Andersen and T. L. Loucks, *Phys. Rev.* **161**, 551 (1968).

<sup>11</sup> R. L. Cohen, *Rev. Sci. Instr.* **37**, 260 (1966); **37**, 957 (1966).

The absorber was made by evaporating, in an ultra-high vacuum system, commercially supplied "triple-distilled" Eu metal onto an outgassed beryllium disc. The Eu layer, about  $50\text{ mg/cm}^2$  thick, was then covered with a layer of evaporated aluminum before being removed from the vacuum. This effectively prevented oxidation of the Eu during transfer between the evaporator and the measuring cryostat. Three absorbers were made, sequentially, during a single evaporation and they appeared to have identical Mössbauer spectra.

The hf spectra (see Figs. 1 and 2) showed no sign of any precipitated impurity, such as  $\text{Eu}_2\text{O}_3$ ,  $\text{EuO}$ , or

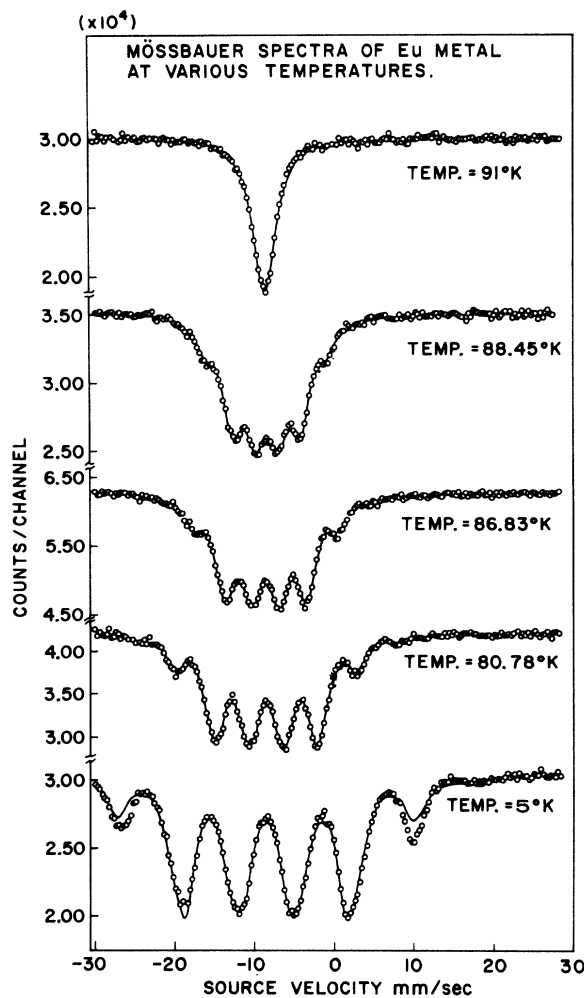


FIG. 1. Spectra of Eu metal above and below  $T_i$ . The hfs below the ordering temperature is directly displayed and is proportional to the observed splitting. Each spectrum consists of 18 lines, not all of which are resolved. The solid line is the best fit to the observed points, using line positions and intensities constrained using the known properties of the Eu hf spectrum. The internal field is determined with a precision of about 0.1-0.2% ( $1\sigma$  error limits). The differences between the data and least-squares curve (visible especially in the  $5^\circ$  data) result primarily from the fact that the absorber is so thick that saturation effects are significant, and the thin-absorber line intensities used for the theoretical curve are not exactly valid.

EuH<sub>2</sub>. The spectra are very sensitive to the presence of such impurities, since all are paramagnetic at the temperature used in this experiment (and therefore they have sharp intense, single lines). They also have higher Debye temperatures and, therefore, higher recoil-free fractions than the metal, so that their lines appear relatively stronger. The Mössbauer spectra are less sensitive to the existence of such possible dissolved impurities as Ca, Yb, and H. However, the sharpness of the transition observed (see Figs. 3 and 4) and the good agreement between our  $T_t$  and the temperature of the specific-heat peak for the high-purity sample in

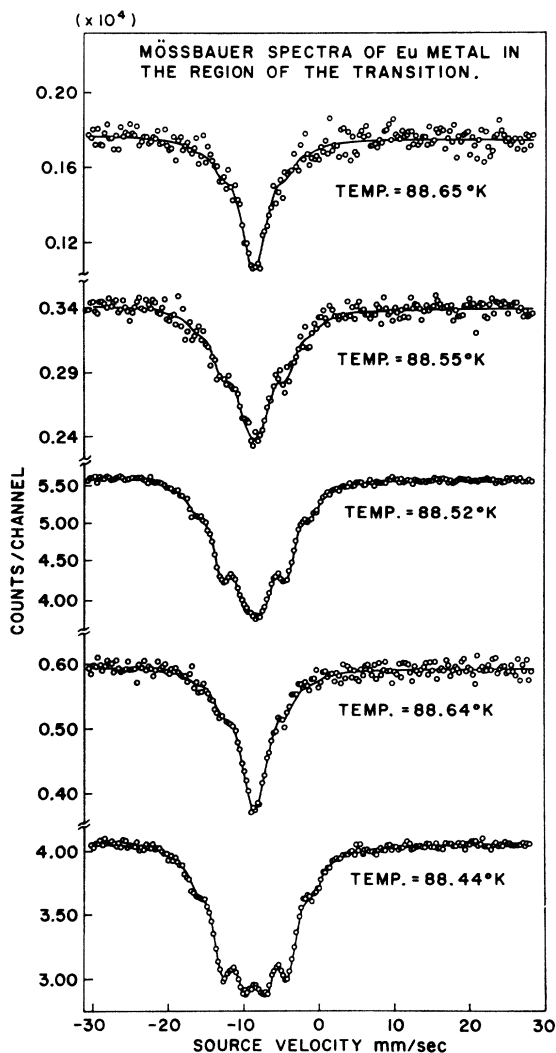


FIG. 2. Spectra of Eu metal in the temperature region of the phase transition. The spectra are shown (from the top) in order of the time at which they were taken. The solid line is the result of a least-squares fit assuming that the absorption resulted partly from a "split" spectrum like those in Fig. 1 and partly from a single line. This is equivalent to the assumption that paramagnetic Eu (unsplit spectrum) and ordered Eu (split) coexist over a narrow temperature range. Parameters evaluated from the least-squares fits are plotted in Figs. 4 and 5.

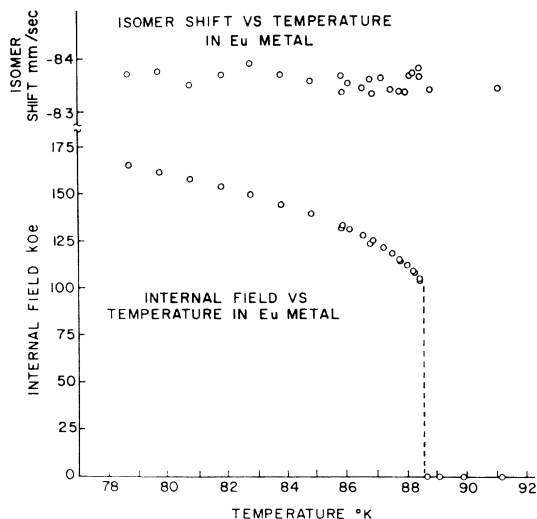


FIG. 3. (a) Observed internal fields plotted as a function of temperature. Note the sudden drop of the field at  $T_t$ . The ( $1\sigma$ ) error flags are about the size of the points. (b) Observed isomer shifts as a function of temperature. Note that there is no substantial discontinuity at  $T_t$ . Isomer-shift values are relative to an Eu<sub>2</sub>O<sub>3</sub> absorber at 78°K.

Ref. 5 suggest that the evaporated layer consisted of very pure Eu.

The Eu-coated beryllium disc was mounted in a copper ring with clamp screws, using silicone grease to improve thermal contact. The copper ring was surrounded by a radiation shield which was in thermal contact with it and this whole assembly was surrounded by a shield held at about 80°K during the measurements. The absorber holder was thermally connected to a liquid-nitrogen bath through a polyester heat leak, and heated by small resistors to reach the desired temperature. The temperature was measured by a differential thermocouple (Au-2.1%Co versus Cu) with the refer-

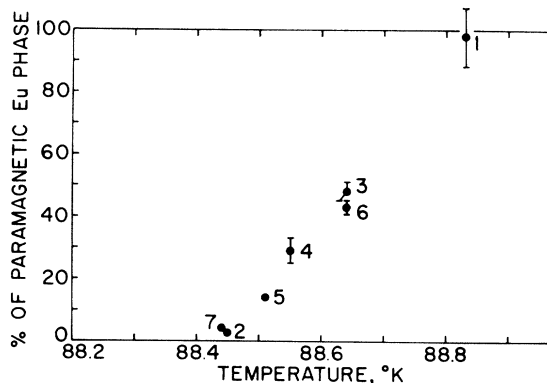


FIG. 4. Ratio of the areas of the ordered and paramagnetic parts of the absorption spectra in the transition region. The points are numbered in the order in which the runs were made. The figure shows clearly the absence of hysteresis. The total transition width is about 0.3°K. The transition width and temperature appear to lie intermediate between those for the two samples used in Ref. 5. (See Fig. 7.)

ence junction in contact with a bath of pure liquid nitrogen. The temperature variations of the reference bath with barometric pressure were taken into account. The thermocouple output was bucked by a voltage corresponding to the desired absorber temperature, and the resulting error signal was amplified and fed to the resistors mounted on the copper ring. This system provided simple, stable, proportional control. The over-all long-term stability and resetability was  $0.03^\circ\text{K}$  and was somewhat better for short measurements. These estimates are confirmed by the small scatter of the results. An additional over-all check and an absolute calibration at the boiling point of liquid oxygen were provided by a Cu-Constantan thermocouple (with  $273.16^\circ\text{K}$  reference junction). The absolute calibration accuracy of the temperature scale is estimated to be better than  $0.3^\circ\text{K}$ .

### B. Results of Mössbauer-Effect Measurements

The resulting spectra taken at  $88.45^\circ\text{K}$  and below were analyzed for hf field and isomer shift by least-squares fitting,<sup>12</sup> and the results are shown in Figs. 3 and 5 and in Table I. The calculated hf spectrum was highly constrained by the known properties of the  $\text{Eu}^{151}$  nuclear-level scheme, and contained only the over-all magnetic hf splitting, isomer shift, and linewidth (assumed identical for all 18 lines in the spectrum) as significant free parameters. The good linewidths ( $\sim 3$  mm/sec, FWHM) and generally good fit between calculated and experimental spectra show that relaxation of the Eu-ion moments was fast enough to provide a well-averaged hf field at the Eu nucleus. Thus, the hf

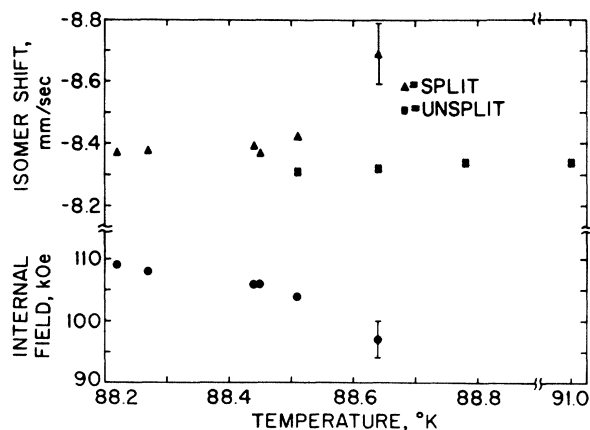


FIG. 5. Internal fields and isomer shifts obtained from the least-squares fits shown in Fig. 2. Error bars shown are  $1\sigma$ ; where no errors are indicated, they are about the size of the points. The fact that in the transition region the paramagnetic and ordered parts of the spectrum have noticeably different isomer shifts is discussed in the text. Note that the  $H_{\text{int}}$  of the split spectrum changes only very slightly in the transition region.

<sup>12</sup> We are indebted to Dr. C. S. Roberts and Dr. C. Reinsch for general purpose least-squares fitting programs.

splitting is proportional to the time-averaged hf field and, to a good approximation, to the sublattice magnetization. This fact will be used later in the discussion.

The temperature region just above  $88.45^\circ\text{K}$  shows spectra (Fig. 2) which appear to be a combination of "split" spectra from magnetically ordered Eu with approximately the same hf field as the  $88.45^\circ\text{K}$  spectrum, and a single line from paramagnetic Eu. This is exactly what would be expected if a variation in  $T_i$  through the absorber (resulting from strain or an inhomogeneous distribution of impurities) resulted in the coexistence of ordered and disordered phases over a narrow temperature range. To attain good fits, it was necessary to allow the "split" and "unsplit" spectra to have independent isomer shifts. This is discussed

TABLE I. Internal fields and isomer shifts in Eu at various temperatures. Indicated errors are  $\sim 1\sigma$  and represent only the precision of the data, arising primarily from statistical effects. Absolute (calibration) error is less than 3%. Isomer shift is relative to  $\text{Eu}_2\text{O}_3$  at  $78\text{zK}$ .

Temp	$H_{\text{eff}}$ (kOe) ( $\pm \sim 0.3$ kOe)	Isomer shift (mm/sec) ( $\pm 0.02$ mm/sec)
5	257.2	8.36
78.74	164.7	8.37
79.74	161.5	8.38
80.78	158.0	8.35
81.82	154.6	8.37
82.81	149.6	8.39
83.82	144.9	8.37
84.83	139.6	8.36
85.86	133.0	8.37
85.89	132.7	8.35
86.07	131.8	8.35
86.56	128.0	8.34
86.83	125.2	8.36
86.90	125.8	8.33
87.22	122.0	8.36
87.53	118.8	8.34
87.84	115.0	8.34
87.85	114.5	8.32
88.02	113.1	8.34
88.22	109.4	8.37
88.27	108.1	8.37
88.44	104.5	8.38
88.45	105.2	8.36

below. As can be seen in Fig. 2, an analysis based on this model is very successful in explaining the observed spectra. This emphasizes the fact that there is a unique smallest field, essentially the value obtained at  $88.45^\circ\text{K}$ , from which the hf field goes discontinuously to zero as the material becomes paramagnetic. The plot of the relative intensities of the paramagnetic and ordered components (Fig. 4) shows us the width of the transition; the value of about  $0.3^\circ\text{K}$  in our absorber is slightly greater than the width of about  $0.2^\circ\text{K}$  observed for the specific-heat peak in the better of the two samples studied by Gerstein *et al.*<sup>5</sup> The curve of paramagnetic fraction versus temperature shown in Fig. 4 does not depend on the thermal history of the sample; thus, to the time scale of the shortest runs (about 10 min long), we can say that no hysteresis was observed. The

temperature control was free of any overshoot which might have promoted equilibration.

#### IV. THERMAL-EXPANSION MEASUREMENTS

The differential thermal expansion of a bulk polycrystalline sample of Eu was studied using a standard three-terminal capacitance technique.<sup>13</sup> The sample was taken from the same block used to provide the Eu for making the evaporated absorbers for the Mössbauer experiments. The width and temperature (about 2° lower than  $T_i$  measured for the samples made by distillation) of the anomalous thermal-expansion region, shown in Fig. 6, suggest that the nominally "99.9% pure" material contained substantial impurities; this was confirmed by chemical analysis. These impurity problems, plus the polycrystalline nature of the sample, make an exact quantitative analysis of the data im-

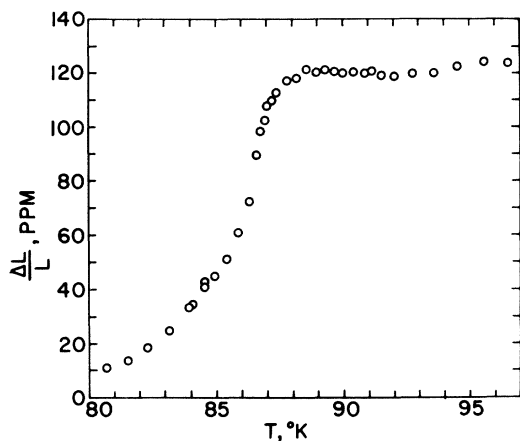


FIG. 6. Differential expansion in the vicinity of  $T_i$  for a piece of bulk, polycrystalline Eu metal about  $3 \times 3 \times 20$  mm long. A constant slope of 20 ppm/°K representing the sample cell expansion plus the normal Eu thermal expansion has been subtracted to emphasize the anomaly.

possible, but we can use the measurements to make certain estimates. Of the  $\Delta L/L$  change shown in Fig. 6, we consider that about 70 ppm can be attributed to the first-order part of the transition. This corresponds to a volume change of 210 ppm if we assume that the length change of the polycrystalline sample represents a reasonable average of the lattice constant changes so that  $\Delta V/V = 3\Delta L/L$ . The remaining 50 ppm of the  $\Delta L/L$  change, presumably, results from the magnetostriction due to the increase of magnetization between the transition temperature and 80°K.

#### V. DISCUSSION

##### A. First-Order Transition

From Fig. 3, it can be seen that at about 88.6°K the hf field suddenly drops to zero from 40% of its

<sup>13</sup> G. K. White, *Cryogenics* **1**, 151 (1961).

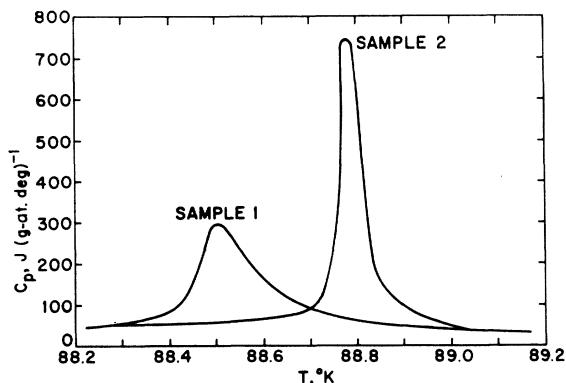


FIG. 7. Curves showing approximate behavior of the specific heat of two samples of Eu, taken from data reported by Gerstein *et al.*, Ref. 5. It is clearly seen that the width and the position of the specific-heat peak at  $T_i$  depends strongly on the quality of the sample (sample II was the purer of the two). The sharpness of the peak in sample II is also a strong indication for the first-order transition.

saturation value. This discontinuity is characteristic of a first-order phase transition. To our knowledge, this is the first time that it has been suggested that the anti-ferromagnetic-to-paramagnetic phase transition in Eu metal is of first order. The findings of our experiments are substantiated by very recent specific-heat measurements,<sup>5</sup> which reveal a very sharp peak, in just this temperature regime (see Fig. 7). The total latent entropy of the transition observed by Gerstein *et al.* in this work was 2.7 J/g-at. deg. Assuming that the sublattice magnetization is proportional to the hf field and goes from 40% of saturation to zero, one calculates a magnetic entropy change (using  $S = \frac{7}{2}$  and the results of Ref. 14) of 1.7 J/g-at. deg. This indicates a lattice entropy change of about 1 J/g-at. deg. It should be emphasized that the specific-heat measurements, in agreement with our results, showed no hysteresis. Two aspects of the observed first-order transition have to be emphasized: First, to date, no change of the lattice constants of Eu metal has been detected with x-rays in the vicinity of the transition.<sup>15</sup> This is consistent with the results of the thermal-expansion measurements described above; because the x-ray measurements usually only detect changes in the lattice constant down to  $\Delta L/L = 10^{-4}$ , they could not find the small change taking place in Eu metal which we measured by the thermal-expansion technique. Second, the constancy of the isomer shift (*IS*), in going through the critical temperature, shows that there is no change in valence connected with the first-order transition. Note

<sup>14</sup> C. P. Bean and D. S. Rodbell, *Phys. Rev.* **126**, 104 (1962). Recently, a first-order transition in  $\text{ErCo}_2$  has been explained in terms of this model [G. Petrich and R. L. Mössbauer, *Phys. Letters* **26A**, 403 (1968); G. Petrich, *Z. Physik.* (to be published)].

<sup>15</sup> C. S. Barrett, *J. Chem. Phys.* **25**, 1123 (1956). Low-temperature x-ray diffractometer measurements made here by Dr. H. J. Levinstein on the samples we used in our measurements revealed no significant anomalies.

that though the  $IS$  values above and below the transition region are the same (see Figs. 3 and 5), there is a small but significant difference between  $IS$  values for the split and unsplit spectrum components in the transition region.<sup>16</sup>

There are a number of mechanisms that have been discussed recently that can cause a magnetic transition from the paramagnetic to the magnetically ordered state to be of first order. The models, which have been proposed to explain these transitions, all assume that the free energy of the system under consideration contains another term besides those originating from the usual bilinear exchange Hamiltonian.<sup>17</sup> Additional terms arising from the ground-state energy-level scheme<sup>18</sup> ("Blume mechanism"), quadrupole-quadrupole coupling,<sup>19</sup> or magnetostrictive effects<sup>14,20,21</sup> have been discussed. Of these mechanisms, the "Blume mechanism,"<sup>18</sup> the quadrupole-quadrupole coupling,<sup>19</sup> and the cooperative spin-lattice coupling<sup>22</sup> can be ruled out immediately in the present case because of the  $^8S_{7/2}$  (spin only) ground state of the Eu ions in Eu metal.

The large observed anisotropy fields<sup>7</sup> suggest a large crystalline anisotropy and, therefore, seem to be at variance with the previous statement. Yet, it has been shown that spiral magnetic structures can result from isotropic-exchange interactions if the exchange integrals, between ions in the  $nm$  planes and the  $nmn$  planes, have certain ratios<sup>23,24</sup>; these structures can require high applied fields (comparable to or larger than the exchange) to reach magnetic saturation, as is actually observed in the present case. It has been shown for Eu<sup>9</sup> that exchange interactions extend over large distances, so that coupling to  $nmn$  planes (and beyond) should be important.

Therefore, we have to assume that either biquadratic exchange<sup>25</sup> or a strong dependence of the net exchange

on the lattice parameters<sup>14,20,21</sup> must be responsible for the first-order transition in Eu metal. We are inclined to believe that the second is actually the case—for reasons which will be outlined now. In the simple approach outlined by Herpin *et al.*<sup>23</sup> to explain the development of a spiral structure without any crystal-line anisotropy, the turn angle  $\alpha$  of the spiral is essentially given by the ratio  $J_1/J_2$ , where  $J_1$  and  $J_2$  are the exchange integrals to the  $nm$  and  $nmn$  layers, respectively. (The extension to cases where exchange to more distant planes must be considered is obvious.) Since the neutron-diffraction results show that the turn angle changes in approaching the critical temperature, it has to be assumed that the relative magnitudes of the exchange integrals change, i.e., there is a temperature-dependent exchange integral. This is the mechanism used by Bean and Rodbell<sup>14</sup> and also by Lines and Jones.<sup>21</sup> These two treatments are roughly parallel, except that the first considers isotropic lattice changes and the second, distortions from ideal symmetry.

The variation of the Eu ordering temperature and lattice constant with pressure have been obtained by Grazhdankina and McWhan *et al.*<sup>26</sup> These data are adequate to calculate, using the theory of Bean and Rodbell,<sup>14</sup> the "criticality parameter" (proportional to the compressibility times the square of the volume derivative of the transition temperature) for the transition; this value is far too small to produce a first-order transition in the (isotropic) model they consider. The small value of  $\Delta V/V$  ( $\approx 200$  ppm), determined from our thermal-expansion results, provides further confirmation of this conclusion. We, therefore, consider a distortion of the lattice with temperature to be the likeliest cause of the change of the exchange interaction with temperature. This is a situation very similar to that observed in MnO and interpreted by Lines and Jones.<sup>21</sup> In Eu, however, the situation is particularly complex in that, because the distortion is caused by the (helical) magnetization, the distortion itself should be a helix in the lattice.

It should be pointed out, in addition, that it is very unlikely that a crystalline anisotropy is responsible for the change in turn angle with temperature, though this is the case with other rare-earth metals. Eu<sup>2+</sup>, being in a  $^8S_{7/2}$  ground-state configuration, has only a very small orbital contribution to its ground-state wave functions induced by higher-order mechanisms. It has also been found that the anisotropy field in EuO, which is a cubic ferromagnet with a Curie temperature of 69°K, has a magnitude of only a few hundred oersteds<sup>27</sup>; this again reflects the lack of orbital contributions to the ground-state wave functions of the Eu<sup>2+</sup> ions.

It might be argued that the sudden vanishing of the

<sup>16</sup> The likeliest cause for this would seem to be that a dissolved impurity that changes  $T_t$  also changes the  $IS$ . Thus, part of the absorber having a large impurity concentration (and therefore, e.g., a low  $T_t$ ) would have a different  $IS$  from that of a purer absorber segment. Well above and below  $T_t$  (since the  $IS$  difference is very much smaller than the 3-mm/sec linewidth), an "average"  $IS$  is observed. In the transition region, however, the difference in splittings allows discrimination of "high- $T_t$ " and "low- $T_t$ " material with detection of the different isomer shifts. This analysis supports the view that inhomogeneous dissolved impurities, rather than strain, are the principal source of the transition broadening.

<sup>17</sup> D. T. Teaney, in *Conference on Phenomena in the Neighborhood of Critical Points*, Washington, D. C., 1965, edited by M. S. Green and J. V. Sengers (U. S. Government Printing Office, Washington, D. C., 1966), p. 50; see also F. B. Anderson and H. B. Callen, *Phys. Rev.* **136**, A1068 (1968).

<sup>18</sup> M. Blume, *Phys. Rev.* **141**, 517 (1966).

<sup>19</sup> M. Blume and Y. Y. Hsieh, *J. Appl. Phys.* **40**, 1249 (1969).

<sup>20</sup> M. E. Lines, *Phys. Rev.* **139**, A1304 (1965).

<sup>21</sup> M. E. Lines and E. D. Jones, *Phys. Rev.* **139**, A1313 (1965).

<sup>22</sup> S. J. Allen, *Phys. Rev.* **167**, 492 (1968).

<sup>23</sup> A. Herpin, P. Meriel, and J. Villain, *J. Phys. Radium* **21**, 67 (1960).

<sup>24</sup> U. Enz, *J. Appl. Phys.* **32**, 22S (1961).

<sup>25</sup> D. S. Rodbell, I. S. Jacobs, J. Owen, and E. A. Harris, *Phys. Rev. Letters* **11**, 10 (1963).

<sup>26</sup> N. P. Grazhdankina, *Zh. Eksperim. i Teor. Fiz.* **52**, 397 (1967) [English transl.: *Soviet Phys.—JETP* **25**, 258 (1967)]; D. B. McWhan, P. C. Souers, and G. Jura, *Phys. Rev.* **143**, 385 (1966).

<sup>27</sup> J. F. Dillon and C. E. Olsen, *Phys. Rev.* **135**, A434 (1964).

hf field is caused by relaxation effects.<sup>28</sup> This is very unlikely. Down to about 0.4 of the saturation field, we observe well-resolved spectra corresponding to a unique hf field. This means that the Eu-ion relaxation rate is fast enough to average over the various exchange-split ground-state energy levels. If the relaxation slowed down severely near  $T_i$ , this would show up in a broadening of the lines and in Mössbauer-absorption patterns consisting of complex broad spectra. Since we see no evidence of this, we can rule out the possibility of relaxation effects contributing to the shape of the observed spectra around  $T_i$ .

We can use the Clausius-Clapeyron equation in the form  $dT_i/dP = \Delta V/\Delta S$  to relate the volume change determined from the thermal-expansion results to the entropy change and pressure dependence of the first-order transition temperature. Using our value of  $\Delta V/V = 2.1 \times 10^{-4}$  and Gerstein's<sup>5</sup> value of  $\Delta S = 2.7 J$  (g-at.  $^{\circ}\text{K}$ )<sup>-1</sup>, we get  $dT_i/dP = 2.2 \times 10^{-4} \text{ }^{\circ}\text{K cm}^2/\text{kg}$ ; this is in poor agreement with the value  $dT/dP = 9 \times 10^{-4}$  directly obtained by Grazhdankina.<sup>26</sup> However, a careful examination of the original data presented in that work shows that a value of  $dT/dP$  as low as  $\sim 3 \times 10^{-4}$  can not be rigorously excluded. The remaining discrepancy could easily result from the possibility mentioned before that the  $\Delta L/L$  measurement on a bulk polycrystalline sample may not give an accurate result for  $\Delta V/V$ .

One further aspect of this transition warrants mention: If it indeed results from the interaction of the exchange and lattice constant, the decreasing deformability of the lattice with increasing pressure should eventually eliminate the first-order character at high enough pressure. This would imply a phase-separation line which simply "stops" in the  $T$ - $P$  plane; a situation which is unusual in solids. This elimination of the first-order transition with pressure can also explain the strong nonlinearity observed in  $dT_N/dP$  in the following way: The recent articles<sup>26</sup> on the variation of the Eu magnetic ordering temperature with pressure show that the magnetic transition temperature rises for applied pressures of a few kbar, levels off at about 10–20 kbar, and then decreases slowly at higher pressures. This low-pressure behavior is different from that observed in the heavy rare-earth metals; in these,  $T_N$  decreases roughly linearly with pressure over a wide range. It seems reasonable to suggest that the rapid increase in ordering temperature observed at low pressures results from a change in  $T_i$  with pressure, and at about 10–20 kbar, the first-order transition gets "squeezed out" by the increasing rigidity of the lattice. Then, above 20 kbar, the "normal" decrease of  $T_N$  with pressure is observed.

<sup>28</sup> M. Blume, *Hyperfine Structure and Nuclear Radiations*, edited by E. Matthias and D. A. Shirley (North-Holland Publishing Co., Amsterdam, 1968), p. 911.

## B. Critical Parameters

It has been shown, both experimentally and theoretically,<sup>1</sup> that in magnetic systems having a paramagnetic to magnetically ordered state transition which is of second order, the sublattice magnetization  $M$  in the vicinity of the critical temperature  $T_c$  can be described by the relation

$$M = M_0 D (1 - T/T_c)^\beta, \quad (1)$$

where  $D$  is a reduction factor matching this high-temperature formula onto the 0°K magnetization  $M_0$ , and  $\beta$  is called the "critical exponent." There are so far no exact criteria as to the ranges of  $m$  and  $T$  for which this description is accurate. If we assume that the hf field is directly proportional to the sublattice magnetization, we can write Eq. (1) as

$$H = H_0 D (1 - T/T_c)^\beta. \quad (2)$$

It should be recognized that the analysis here, in terms of critical-point theory, is of very limited validity because the transition is, in fact, first order. Additionally, in the present case, an analysis of the data in terms of Eq. (2) clearly can only be done for  $H \geq 0.4H_0$ . We have arbitrarily selected values from the data taken between  $H = 0.4H_0$  and  $H = 0.5H_0$  and least-squares fitted Eq. (2) to them, and shown the results in Fig. 8 and Table II. For the purposes of comparison, the table shows results obtained when the analysis is done over different temperature ranges. It can be seen that  $\beta$  decreases noticeably as points closer to the transition are chosen. At the  $T_i$  itself, the functional

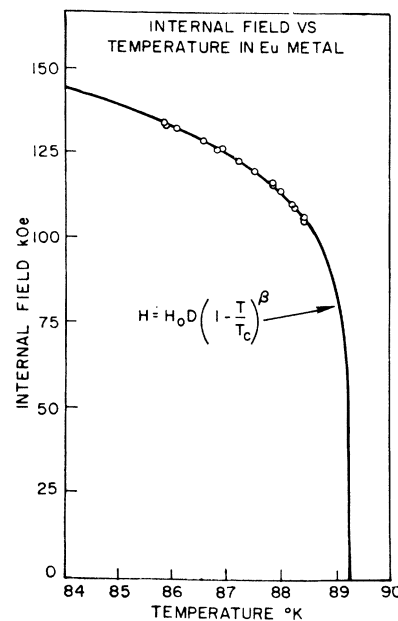


FIG. 8. Fit of the  $H = H_0 D (1 - T/T_c)^\beta$  to hf fields just below  $T_i$  ( $0.4 \leq H/H_0 \leq 0.5$ ). Parameter values obtained from this fit are shown in Table II.

TABLE II. Parameters resulting from least-squares fitting Eq. (2) to the data points over the temperature range (from  $T_{\min}$  to  $T_{\max}$ ) shown. Only statistical ( $1\sigma$ ) errors are shown. Note that the apparent value of  $\beta$  decreases as points closer to the transition are used.

$T_{\min}$ ( $^{\circ}\text{K}$ )	78.5	78.5	81.5	85
$T_{\max}$ ( $^{\circ}\text{K}$ )	88.0	88.5	88.5	88.5
$\beta$	$0.211 \pm 0.008$	$0.198 \pm 0.007$	$0.191 \pm 0.009$	$0.163 \pm 0.031$
$H_0D$ (kOe)	$256 \pm 4.2$	$250 \pm 3.3$	$245 \pm 5$	$224 \pm 10$
$T_N$ ( $^{\circ}\text{K}$ )	$89.86 \pm 0.16$	$89.58 \pm 0.10$	$89.49 \pm 0.12$	$89.23 \pm 0.15$

dependence, of course, corresponds to Eq. (2) with  $\beta=0$ . Although the errors shown in the table appear larger than the variation in  $\beta$ , it must be remembered that the calculations for different temperature ranges were done using many of the same data points, so that the variation of  $\beta$  with temperature range is more significant than the stated error would indicate.

The value for the critical exponent  $\beta$  reported here is rather low and similar values have only been found so far in some low-temperature antiferromagnets ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $T_c = 4.3^{\circ}\text{K}$ ,  $\beta = 0.25$ <sup>29</sup>;  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $T_c = 2.3^{\circ}\text{K}$ ,  $\beta = 0.20$ <sup>30</sup>; DAG,  $T_N = 2.5^{\circ}\text{K}$ ,  $\beta = 0.27 \pm 0.01$ ).<sup>31</sup> In most other cases,  $\beta$  seems to have a value in the range 0.3–0.35. The small value of  $\beta$  in our case, presumably, results from the above-reported first-order magnetic transition. Obviously, the interactions which eventually make the transition first order are already effective below the critical temperature and tend to lower the value of  $\beta$ .

In the case of Eu, the existence of the first-order transition makes it obvious that the assumptions implicit in an analysis in terms of critical-point theory are not fulfilled. The interactions producing the first-order behavior in Eu are, in general, present in magnetic systems, though they are not usually strong enough to destroy the continuous nature of the ordering transition. The state of our knowledge is such that we can not, in general, adjust for such perturbations. Thus, any system which appears to have an anomalously low value of  $\beta$  should be tested carefully for the possibility that weak temperature-dependent terms in the magnetic coupling Hamiltonian, rather than a breakdown of critical-point theory, might be responsible.

<sup>29</sup> N. J. Poulis and G. E. G. Hardemann, *Physica* **19**, 391 (1953), as restated in Ref. 1.

<sup>30</sup> E. Sawatzky and M. Bloom, *Can. J. Phys.* **42**, 657 (1964); W. van der Lugt and N. J. Poulis, *Physica* **26**, 917 (1960), as restated in Ref. 1.

<sup>31</sup> J. C. Norwell, W. P. Wolf, L. M. Corliss, J. M. Hastings, and R. Nathans, *J. Appl. Phys.* **39**, 1232 (1968).

## VI. SUMMARY

A careful study of the hf interactions in Eu metal in the temperature regime from 78 to 90°K has been performed by using the Mössbauer effect. At  $(88.6 \pm 0.3)^{\circ}\text{K}$ , the hyperfine field goes from 40% of saturation to zero, indicating a first-order antiferromagnetic to paramagnetic transition in Eu metal at that temperature. Possible reasons for the occurrence of this first-order transition have been discussed and it seems most likely that it is caused by magnetostrictive effects. These effects must involve a lattice distortion similar to that observed in MnO because the isotropic volume change is too small to account for the transition.

In addition, an attempt was made to analyze the temperature dependence of the hf field between  $0.4H_0$  and  $0.5H_0$  in terms of the equation  $H_0D(1-T/T_N)^\beta$ . This yielded a value of  $\beta = 0.16 \pm 0.04$ , which is very much smaller than the usual reported  $\beta = \frac{1}{3}$ . Because of the relatively high value of  $H/H_0$  and also the proximity of the first-order transition, no further discussion of this low value of  $\beta$  can be made.

## ACKNOWLEDGMENTS

We would like to acknowledge technical advice and comments from Dr. G. K. Wertheim concerning the particular problems of measurement, analysis, and discussion of critical-point phenomena. We are greatly indebted to Dr. E. Helfand for theoretical discussions on the comparison of the results with critical-point theory, and to Dr. M. E. Lines for helpful discussions on magnetostrictive first-order transitions. We performed the thermal-expansion measurements using equipment belonging to Dr. E. Fawcett, and we would like to thank him both for making the apparatus available and for helpful comments on the analysis of the data. The approach in Sec. V reflects comments and suggestions by Dr. M. Blume.