

## Magnetic Structure of Europium\*

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Neutron diffraction experiments on metallic europium have been conducted over a temperature range from room temperature to 4°K using a sample in the form of europium filings. The data show that the metal undergoes a transition to an antiferromagnetic state at a Néel temperature  $T_N$  of 91°K and that this ordering process continues until saturation develops at about 20°K. A model which conforms to the data consists of a helical spin structure with the magnetic moments lying parallel to a cube face and with the rotation axis directed perpendicular to the moments or along the [100] direction. The pitch of the helix was observed to change very slightly with temperature; the period was  $3.5a$  at  $T/T_N=1$  and increased to  $3.6a$  at  $T/T_N=0.05$  where  $a$  is the lattice spacing. On the basis of the above model and the intensities of the magnetic reflections, the calculated ordered moment at each atom site is  $5.9 \pm 0.4 \mu_B$  per atom. This measured moment is somewhat less than the maximum theoretical value of  $7 \mu_B$  expected from divalent europium characterized by a spin only ground state of  $^8S_{7/2}$ . Values of magnetic moment times magnetic form factor,  $\mu f$ , as calculated from Eu coherent magnetic reflections are in agreement with similar values of  $\mu f$  derived from the compound EuO. The intensities of the magnetic diffraction peaks deviate from a Brillouin behavior and instead follow a temperature dependence proportional to  $(T_N - T)^{1/2}$  over a considerable region below the Néel temperature. The Debye temperature, as derived from the nuclear peak intensities, exhibited a variation from 70 to 120°K over a corresponding sample temperature range of 100 to 293°K.

### INTRODUCTION

THE following paper describes additional experimental work on the magnetic properties of europium as obtained from neutron diffraction data. The major findings of the current investigation have already been presented in a brief abstract<sup>1</sup>; however, the present article amplifies and supports the conclusions outlined in the abstract. The current work on Eu represents an improvement over previous diffraction data<sup>2</sup> in that a better sample in the form of metal filings has been used. The metal foil sample employed in the earlier experiment showed a high degree of preferential orientation probably caused by repeatedly rolling the metal to the required small thickness. As a result, information on the ordered moment and magnetic form factor which depend upon correct diffraction peak intensities could not be derived from the initial data. The present powder sample showed no preferred orientation effects and has provided additional knowledge concerning the magnetic structure of europium.

### EXPERIMENTAL

The Eu powder sample had an area density of 0.135 g/cm<sup>2</sup> and was prepared by filing (in an atmosphere of helium) a small casting of the 99% pure metal obtained from the Michigan Chemical Company. The filings were contained in a 3-in.-diam disk-type holder fabricated from Ti-Zr alloy; the holder had a total wall thickness of 0.050 in. and a neutron transmission of 96%. The measured transmission of the Eu sample at a neutron wavelength of 1.391 Å was 23 %; this compared

well with a calculated transmission of 24%. A rough check on the uniformity of the area density of the sample was made by exposing an x-ray film to the  $\gamma$ -ray activity induced by previously placing the sample and holder in a uniform thermal neutron flux. The film did show density variations but no empty regions were evident; any area not occupied by Eu would also have seriously affected the average neutron transmission. In spite of precautions taken to prevent air from contacting the sample, the Eu filings did show a faint yellow color when removed from the cryostat at the completion of the measurements. As judged from the color, this represented formation of the oxide Eu<sub>2</sub>O<sub>3</sub> rather than EuO.

The neutron diffraction data were obtained by using the sample in transmission at one of the diffractometers at the Omega West Reactor. The monochromatic neutron flux of wavelength 1.391 Å was about 10<sup>6</sup> neutrons/cm<sup>2</sup>-sec at the sample position and the collimated beam had a cross-sectional area of 1½ in. × 1½ in. The cryostat was of the type in which the sample was maintained in an atmosphere of helium for good heat transfer. Thermocouples as well as a calibrated germanium resistance

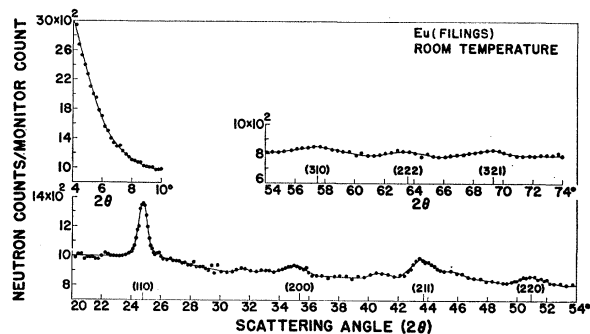


Fig. 1. Neutron diffraction data for Eu at room temperature.

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<sup>1</sup> G. P. Arnold, C. E. Olsen, and N. G. Nereson, *J. Appl. Phys. Suppl.* **35**, 1031 (1964).

<sup>2</sup> C. E. Olsen, N. G. Nereson, and G. P. Arnold, *J. Appl. Phys. Suppl.* **33**, 1135 (1962).

thermometer attached to the Ti-Zr holder were used to measure the Eu temperature. A Ni-powder sample was used to calibrate the diffractometer on an absolute intensity scale.

### DISCUSSION OF RESULTS

A typical room temperature diffraction pattern of the Eu filings sample is shown in Fig. 1. Diffraction peaks providing sufficient intensity for data analysis were obtained from the (110), (211), (220), (310), and (321) reflecting planes. Vertical lines on the abscissa below the reflection plane indices are calculated positions of the Eu peaks using a lattice spacing of 4.582 Å.<sup>3</sup> All of the observed peaks could be identified with the Eu metal lattice except for two peaks of very small intensity on each side of the (211) reflection. The customary semilog plot of the square of the structure factors, as calculated from the diffraction peak intensities, versus  $(\sin^2\theta)/\lambda^2$  is shown in Fig. 2 for a sample temperature of 100°K. The fact that these points fit a straight line and yield the correct Eu scattering amplitude is evidence that the diffraction peaks exhibited the proper intensities and that the sample was not oriented. Towards the end of the five-months data accumulation period, the intensities of all the diffraction peaks had decreased slightly over their initial intensity. This was attributed to slight oxidation of the sample as mentioned previously. These latter data were adjusted to the initial data by a common intensity factor.

The present work confirmed the earlier finding that Eu metal undergoes a transition to an antiferromagnetic state. The Néel temperature for the present powder sample was found to be  $91^\circ \pm 1^\circ\text{K}$  as compared to  $87^\circ\text{K}$  for the rolled foil sample. This temperature difference is probably due to inherent strains in the foil which were induced during the rolling process. The  $91^\circ$  Néel temperature agrees better with the maxima observed in susceptibility measurements.<sup>4</sup> Evidence for the antiferromagnetic state is shown in Fig. 3 which displays a temperature difference diffraction pattern

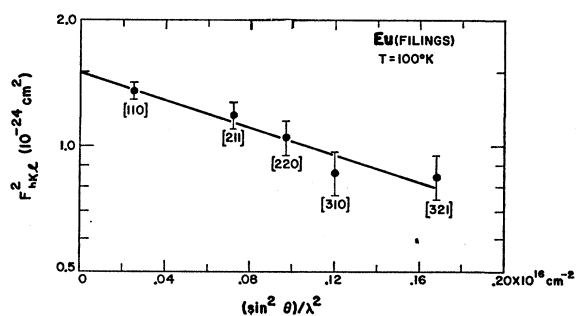


FIG. 2. Square of structure factor versus  $(\sin^2\theta)/\lambda^2$ .

<sup>3</sup> At temperatures of 100°K and less, a lattice spacing of 4.555 Å was used.

<sup>4</sup> R. M. Bozorth and J. H. Van Vleck, Phys. Rev. **118**, 1493 (1960).

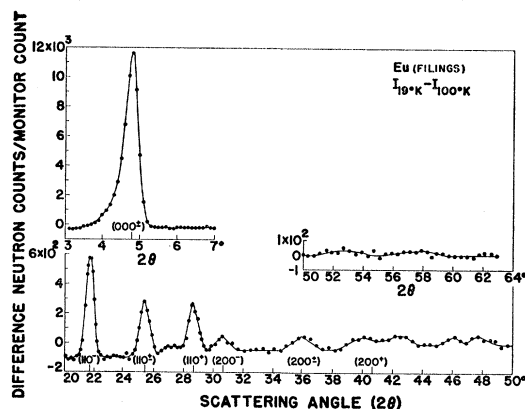


FIG. 3. Temperature difference pattern of Eu illustrating only magnetic scattering.

resulting from subtracting data at 100°K from that at 19°K. The data at 100°K result from only nuclear scattering processes as verified in Fig. 2; the difference pattern in Fig. 3 therefore shows intensities resulting only from magnetic scattering. Salient magnetic features are the intense  $(000^\pm)$  magnetic peak, the two magnetic satellite peaks  $(110^-)$  and  $(110^+)$  on each side of the  $(110)$  nuclear peak position, and also the satellite peaks  $(200^-)$  and  $(200^+)$  surrounding the  $(200)$  nuclear peak position. In a reciprocal lattice space plot, the above satellites are equally spaced from the associated nuclear plane reflections. Different orientations of the crystallites in the sample produce other pairs of satellites such as the  $(110^\pm)$  pairs and the  $(200^\pm)$  pairs which occur close to the  $(110)$  and  $(200)$  nuclear peak positions. Other magnetic satellite peaks occurring at larger scattering angles are not easily identified on account of poorer resolution at large angles and also the reduction in diffraction peak intensity due to the magnetic form factor. Table I summarizes various magnetic data associated with diffraction peak intensities present in the temperature difference pattern of Fig. 3.

The occurrence of pairs of magnetic satellites associated with each nuclear reflection is evidence for either the oscillating component model or the helical spin structure.<sup>5</sup> However, in the helical structure there are

TABLE I. Neutron diffraction data relating to magnetic reflections shown in Fig. 3.

Magnetic reflection	Observed scattering angle	Calculated scattering angle <sup>a</sup>	Observed relative intensity	Multiplicity	Calculated <sup>b</sup> $(\mu f)^2$	$(\sin\theta)/\lambda$ (cm <sup>-1</sup> )
$000^\pm$	4.76°	...	13 000	2	35.8	$0.030 \times 10^8$
$110^-$	21.7°	21.74°	1050	8	20.5	$0.135 \times 10^8$
$110^\pm$	25.4°	25.42°	570	8	23.6	$0.160 \times 10^8$
$110^+$	28.6°	28.65°	505	8	17.5	$0.178 \times 10^8$
$200^-$	30.6°	30.54°	190	2	21.6	$0.189 \times 10^8$
$200^\pm$	36.0°	35.91°	250	8	20.7	$0.222 \times 10^8$

<sup>a</sup> Based upon  $(000^\pm)$  peak position and a lattice spacing of  $a = 4.555$  Å.

<sup>b</sup> Obtained from Eq. (2) in the text.

<sup>5</sup> W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkin-son, Phys. Rev. **126**, 1672 (1962).

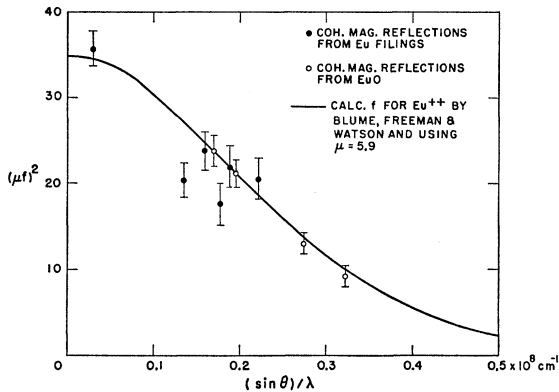


Fig. 4. Comparison of experimental and calculated values of  $(\mu f)^2$  for  $\text{Eu}^{++}$  versus  $(\sin\theta)/\lambda$ .

no extinctions of satellites when  $\sin\theta$  is zero as is the case with the oscillating component model;  $\theta$  is the angle between the spin rotation axis and the scattering vector. The model which best fits the bulk of the data is a helical model with the magnetic moments on each Eu atom lying parallel to a cube face and the axis of the helix directed perpendicular to the moments or along the  $[100]$  direction. In the case of the  $(000^\pm)$  and  $(200^\pm)$  reflections, the angle  $\theta$  is zero and the oscillating component model would predict zero intensity for the above existing satellites.

The expression for the intensity of the helical magnetic satellite peaks has been derived by Koehler.<sup>6</sup> For atoms of only one kind, as in the case of a pure metal, the square of the structure factor is

$$|F_M|^2 = \frac{1}{4} p^2 (1 + \cos^2\theta) (\sin^2\beta) |R|^2 \\ = \frac{1}{4} [(e^2\gamma/2mc^2)gJf]^2 (1 + \cos^2\theta) (\sin^2\beta) |R|^2. \quad (1)$$

Assuming that the magnetic moments in metallic Eu are due to  $\text{Eu}^{++}$  ions, then the ground state is characterized by a spin-only state of  $^8S_{7/2}$  and one can write for the theoretical ordered moment  $\mu = gJ = gS$ . Equation (1) then becomes

$$|F_M|^2 = \frac{1}{16} (0.29 \times 10^{-24}) (\mu f)^2 (1 + \cos^2\theta) (\sin^2\beta) |R|^2, \quad (2)$$

where  $f$  is the magnetic form factor,  $\beta$  is the angle between the moment directions and the moment rotation axis, and  $R$  is the geometrical structure factor of the chemical unit cell. In the present model,  $\beta$  has been chosen as  $90^\circ$ . If  $\beta$  were less than  $90^\circ$  there would be a component of spin along the spin rotation axis and enhancement of the nuclear peak intensities would be observed below the transition temperature; this phenomenon was not observed.

The large intensity of the  $(000^\pm)$  magnetic peak occurring at a scattering angle of  $4.8^\circ$  and the fact that the magnetic form factor  $f$  can be assumed to be unity at this small angle make this peak particularly attractive

for calculating the ordered moment. As indicated in Table I,  $(\mu f)^2 = 35.8$  for the  $(000^\pm)$  peak from which  $\mu = 6.0 \pm 0.4$  Bohr magnetons. This value is lower than the theoretical ordered moment of  $\mu = gS = 7$  Bohr magnetons expected for a  $\frac{7}{2}$  spin state. The lower measured value as compared to the maximum value expected from the metallic  $\text{Eu}^{++}$  ion is also typical of other rare-earth moment measurements.<sup>7</sup> This discrepancy may possibly be accounted for by crystal field interactions. However, one can conclude from the above measurement that the Eu ordered moment in the antiferromagnetic state at  $T < T_N$  is due to the  $\text{Eu}^{++}$  ion rather than the  $\text{Eu}^{+++}$  ion; the latter ion would give a much smaller ordered moment ( $\sim 3\mu_B$ ). Further confirmation that metallic europium is divalent at  $4.2^\circ\text{K}$  is found in the Mössbauer work of Barrett and Shirley.<sup>8</sup>

Values of the product  $(\mu f)^2$  as obtained from other magnetic diffraction peaks possessing sufficient intensity are listed in Table I. Data on values of  $(\mu f)^2$  obtained from the present work on Eu metal as well as  $(\mu f)^2$  values derived from previous data<sup>9</sup> on the compound EuO are displayed in Fig. 4 as a function of  $(\sin\theta)/\lambda$ . These two sets of  $(\mu f)^2$  data should be comparable since the Eu magnetic moment in EuO is due to the  $\text{Eu}^{++}$  ion if one assumes that the oxygen atoms carry no moment. The agreement between the two sets of data for  $(\mu f)^2$  is reasonable except for the Eu metal points at  $(\sin\theta)/\lambda = 0.135$  and  $0.178$  associated with the  $(110^-)$  and  $(110^+)$  satellite peaks. At the present time, it is not clear why the above two satellite peaks deviate considerably from the other data points. Perhaps some slight modification of the basic helical model is indicated or the multiplicities for these satellites are too high.

The magnetic form factor for  $\text{Eu}^{++}$  has been calculated by Blume, Freeman, and Watson.<sup>10</sup> The best fit to the experimental  $(\mu f)^2$  data is obtained if one multiplies the calculated  $f$  values by  $\mu = 5.9$ ; this is well within the experimental error of the value  $\mu = 6$  derived from the  $(000^\pm)$  peak alone. The shape of the calculated magnetic-form-factor curve is in satisfactory agreement with the experimental data. The general consistency of the experimental data and the  $\text{Eu}^{++}$  calculations in Fig. 4 are additional reasons for support of the Eu divalent ion as the magnetic constituent in Eu metal at low temperatures ( $T < T_N$ ).

Experiments on paramagnetic diffuse scattering were carried out on both the present Eu powder sample and the previous rolled foil sample but the results were inconclusive. Diffuse scattering data obtained from regions between diffraction peaks at a temperature of

<sup>7</sup> H. R. Child, M. K. Wilkinson, J. W. Cable, W. C. Koehler, and E. O. Wollan, Phys. Rev. **131**, 922 (1963).

<sup>8</sup> P. H. Barrett and D. A. Shirley, Phys. Rev. **131**, 123 (1963).

<sup>9</sup> N. G. Nereson, C. E. Olsen, and G. P. Arnold, Phys. Rev. **127**, 2101 (1962).

<sup>10</sup> M. Blume, A. J. Freeman, and R. E. Watson, J. Chem. Phys. **37**, 1245 (1962).

<sup>6</sup> W. C. Koehler, Acta Cryst. **14**, 535 (1961).

120°K were subtracted from similar data taken at 19°K. The subtracted results, which are proportional to  $(\mu f)^2$ , showed large variations between several runs; however, the temperature difference pattern was only about 10% of the 19°K background. The rough averaged results did extrapolate, at  $(\sin\theta)/\lambda=0$ , to approximately the same value of  $(\mu f)^2$  as obtained from the coherent peaks in Fig. 4; however, the diffuse scattering data at larger angles yielded a curve which decreased much more rapidly with  $(\sin\theta)/\lambda$  than the coherent reflec-

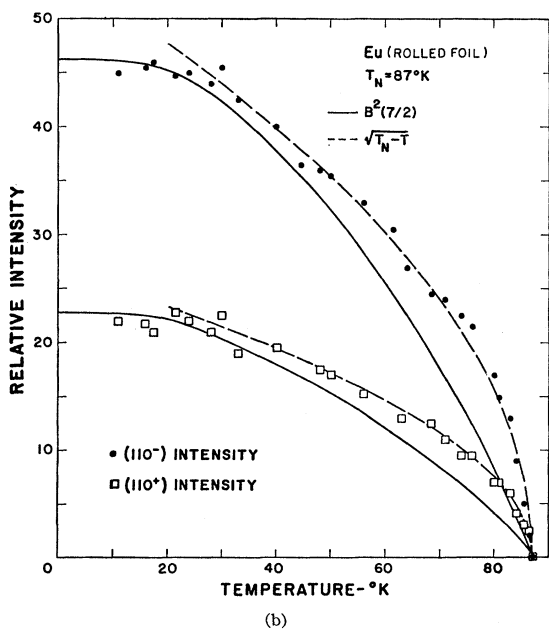
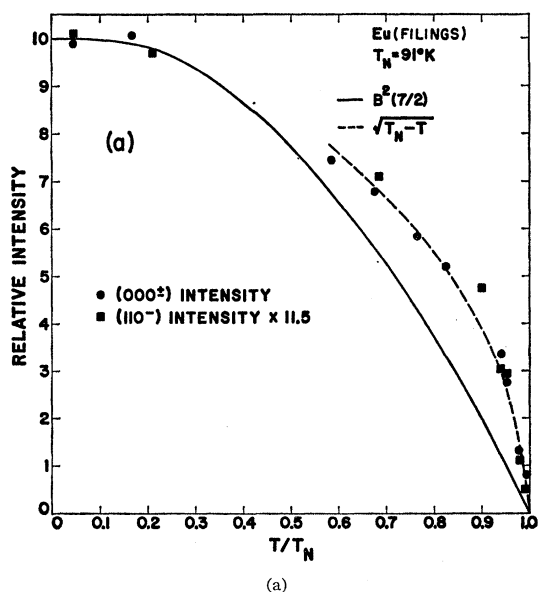


FIG. 5. Intensities of various Eu magnetic reflections versus temperature using a powder sample [Fig. 5(a)] and a rolled foil sample [Fig. 5(b)].

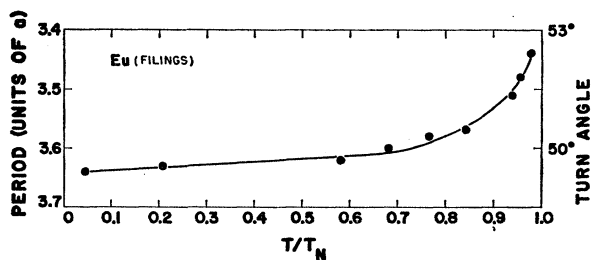


FIG. 6. Interlayer turn-angle variation versus temperature. The right scale gives the helix angle in degrees and the left scale expresses the angle in units of the lattice spacing,  $a$ .

tions. Better data are needed to establish the diffuse scattering curve. One can tentatively conclude from the present data that the presence of the  $\text{Eu}^{++}$  ion is indicated at temperatures above the transition temperature since the diffuse scattering results and the low-temperature coherent reflections show approximately the same value of  $(\mu f)^2$  at small scattering angles. Europium susceptibility measurements<sup>4,11</sup> in the temperature region  $T_N < T < 300^\circ\text{K}$  have given values for the effective magnetic moment,  $\mu_{\text{eff}}$ , in the range from 7.1 to  $8.3\mu_B$ ; these data also support the divalent model in the above temperature range as one would theoretically expect  $\mu_{\text{eff}} = g[J(J+1)]^{1/2} = 7.9\mu_B$  for  $\text{Eu}^{++}$  ions and  $3.5\mu_B$  for  $\text{Eu}^{+++}$  ions. The difference in shape for  $(\mu f)^2$  between the coherent diffraction results and the diffuse scattering data as a function of  $(\sin\theta)/\lambda$  may be due to temperature-dependent interactions between the  $\text{Eu}^{++}$  ions as has been suggested by Arrott.<sup>12</sup>

The earlier data<sup>2</sup> on the Eu foil indicated that the temperature dependence of the magnetic reflections did not conform to a Brillouin function. The present Eu filings data confirm the previous finding. Figure 5(a) displays the neutron intensity of the  $(000\pm)$  and  $(110^-)$  magnetic peaks as a function of the temperature ratio  $T/T_N$  and verifies that the intensity of both peaks is in general higher than the squared Brillouin function calculated for  $S = \frac{7}{2}$  and  $T_N = 91^\circ\text{K}$ . Instead, the intensity of the magnetic peaks varies with temperature according to  $(T_N - T)^{1/2}$  over a considerable region below the Néel temperature. A similar presentation for the Eu foil data shown in Fig. 5(b) exhibits the same temperature dependence.

Perhaps it is not too surprising that the temperature dependence of the magnetic reflections does not conform to  $B^2(\frac{7}{2})$  as other antiferromagnetic materials (e.g., MnO and NiO) also show a similar departure. An attempt was made to fit the present temperature data to the biquadratic exchange interaction postulated by Rodbell *et al.*<sup>13</sup> using values of  $j/J$  in the range from

<sup>11</sup> C. H. LaBlanchetais and F. Trombe, *Compt. Rend.* 243, 707 (1956).

<sup>12</sup> A. Arrott, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, to be published), Vol. II.

<sup>13</sup> R. S. Rodbell, I. S. Jacobs, J. Owen, and E. A. Harris, *Phys. Rev. Letters* 11, 10 (1963).

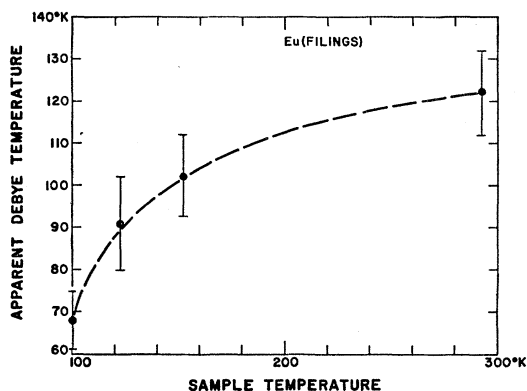


FIG. 7. Debye temperature variation of Eu versus sample temperature.

0.01 to 0.02 but a satisfactory fit was not obtained. The present Eu data lie approximately half-way between a  $B^2(\frac{1}{2})$  curve and the MnO data.

The more complete data of Fig. 5(b) indicate that the intensity of the magnetic reflections undergoes a smooth transition from the onset of ordering until saturation occurs at around 20°K. This behavior is in contrast to many rare earths which have been previously investigated of which the majority show a transition to an antiferromagnetic state (as Eu) and then another transition at a lower temperature to a ferromagnetic state. The Eu data show no second transition above 4°K.

The change of the interlayer turn angle of the helix with temperature was obtained from the scattering angle position of the (000 $\pm$ ) magnetic diffraction peak. This variation is graphed in Fig. 6 and, with the exception of Tm, is observed to exhibit a considerably smaller variation than the rare earths which have been presently investigated.<sup>14</sup> Also, the temperature dependence of the pitch is not proportional to  $T - T_N$  as is true for most of the other rare earths.<sup>14</sup>

DeGennes and Saint-James<sup>15</sup> have shown that the interlayer turn angle of the heavy rare-earth metals

<sup>14</sup> W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkinson, *J. Phys. Soc. Japan* **17**, Suppl. B-III, 32 (1962).

<sup>15</sup> P. G. DeGennes and D. Saint-James, *Solid State Communications* **1**, 62 (1963).

fit a monotonically decreasing curve when plotted as a function of the dimensionless quantity,  $\mu = 1/(2lk_F)$ , where  $l$  is the mean free path and  $k_F$  is the Fermi wave vector. The value of  $\mu$  for Eu is  $3.1 \times 10^{-2}$  as derived from the Eu specific resistivity of  $75\text{-}\mu\Omega\text{-cm}$  in the vicinity of  $T_N$ . Using the above value for  $\mu$  and an interlayer turn angle of  $52^\circ$  at  $T_N$ , it is found that Eu also conforms satisfactorily to the curve shape established by the other rare-earth elements.

The Debye temperature for Eu can be obtained from the nuclear-diffraction peak-intensity data as presented as in Fig. 2. The data shown in Fig. 2 were taken at a sample temperature of 100°K and yield a Debye temperature of about 70°K. Other sample temperatures gave the Debye temperature variation displayed in Fig. 7. Large errors are associated with the Debye temperature measurements but a definite monotonic trend in the values seems to be indicated. The nuclear-peak data varied in a manner such that the intensities at the larger scattering angles increased with increasing sample temperature; the peak intensity at small angles stayed approximately constant. The above type of intensity change would indicate that ferromagnetic ordering above the Néel temperature was not responsible for this apparent variation observed in the Debye temperature. Also, Mossbauer absorption experiments<sup>8</sup> show no splitting of the lines at a temperature of 100°K, indicating the absence of any ferromagnetism for  $T > T_N$ .

The range of Debye temperatures measured for Eu lies considerably below the average data line obtained by graphing the observed Debye temperatures of other rare earths versus atomic number.<sup>16</sup> It is noteworthy to observe that also Yb and Sm exhibit a similar anomalous behavior; Yb is known to be divalent in the metallic state and Sm may also be divalent. Other like physical properties for Eu and Yb, which would dictate similar Debye temperatures, are lower melting and boiling points and higher metallic radii than the other rare earths. The large variation of the Eu Debye temperature is not understood at present. Perhaps temperature dependent interactions of  $\text{Eu}^{++}$  ions may also be involved in this phenomenon.

<sup>16</sup> K. A. Gschneidner, *Rare Earth Alloys* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1961), p. 37.