Neutron Diffraction Studies on EuO*

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Neutron diffraction studies on EuO at various temperatures have been made at a neutron wavelength of 1.391 Å. The experimental data confirm the existence of ferromagnetism in this compound at temperatures below the Curie point (77±1°K). The intensities of the magnetic reflections vary with temperature according to the square of a Brillouin function having a spin of 7/2. The magnetic scattering data also provide information on the magnetic amplitude form factor for Eu^{2+} over the region from $(\sin\theta)/\lambda=0.17$ to 0.32, and indicate that the form factor decreases to half-value at $(\sin\theta)/\lambda = 0.29$. The nuclear scattering data of EuO show that the absolute value of the neutron coherent scattering length for Eu is $|f_{Eu}|=(0.63\pm0.03)\times10^{-12}$ cm; the experimental value for the Eu nonresonant coherent scattering length is $f_0(\mathrm{Eu})=(0.88\pm0.04)\times10^{-12}$ cm.

INTRODUCTION

INVESTIGATIONS by Matthias *et al.*[1] have indicated that EuO is ferromagnetic. Because ferromagnetism is not usually associated with insulating materials or oxides, it seemed desirable to obtain further information on this interesting compound by neutron diffraction experiments. Also, since other work[2] shows that coherent neutron magnetic scattering from the metal Eu does not vary with temperature according to the usual Brillouin behavior, it is of interest to determine if the magnetic scattering from EuO behaves similarly. Another incentive for the present experiment is to extend the information on current investigations on the magnetic amplitude form factor of europium.

EXPERIMENTAL

The europous oxide was prepared by reacting stoichiometric amounts of europium metal and europium sesquioxide. The previously ignited sesquioxide and the europium metal were weighed into a tantalum bomb which was evacuated and welded shut using an electron beam. The bomb was then slowly heated by induction methods in vacuum to 850°C in such a manner as to allow the contents to reach thermal equilibrium. When the contents had reached equilibrium the heating was slowly increased until the temperature reached 1600°C, where it was held for eight hours in order to insure reduction of the oxide. Evidence for the initiation of the reaction could be seen by the glowing of the crucible. The reduced material consisted of purple brown lumps with single crystal areas of ~0.1 mm. Rough electrical resistivity measurements on the lumps gave specific resistivities of the order of $(3\text{–}5)\times10^4$ Ω cm. X-ray diffraction measurements showed it to be a cubic-face-centered material with $a_0=5.142\pm0.002$ Å in agreement with the data reported by Eich *et al.*[3] and Matthias *et al.*[1]

The EuO powder sample used in the experiment weighed 8 g and had an area density of 0.19 g/cm²; this gave a neutron transmission of 15.9%. The sample was contained in a Ti-Zr alloy holder having a total wall thickness of 0.050 in. and a neutron transmission of 96%. A background run taken with the Ti-Zr holder alone showed no diffraction peaks.

The data in this experiment was obtained by using the sample in transmission in one of the neutron diffractometers at the Omega West reactor. The spectrometer is conventional and employs the (111) planes of a single lead crystal to produce a flux of about 10^7 neutrons/cm²-sec at the sample position. The neutron wavelength is 1.391 Å. The cryostat in use is similar to that described by Barrett.[4] The temperature of the EuO powder was obtained from four thermocouples attached to the Ti-Zr holder.

RESULTS

Magnetic Scattering of EuO

The neutron diffraction data obtained from the EuO powder sample at room temperature is shown in Fig. 1(a). Diffraction peaks from the (200), (220), (222), and (400) reflection planes are clearly evident, and there also is an indication of a small peak from the (111) plane. Confirmation of ferromagnetism in EuO at low temperatures is shown by the diffraction pattern at $T=28$°K in Fig. 1(b); all of the nuclear peaks observed at room temperature increase in magnitude at the lower temperature. At this lower temperature the (111) reflection is greatly increased and the (311) reflection, which was not observable at room temperature, is now obvious. It was not practical to utilize the (400) reflection for magnetic studies on account of its small magnitude. The fact that the magnetic diffraction peaks occur at the same position as the nuclear scattering peaks proves that the magnetic unit cell is the same size as the ordinary chemical unit cell.

The neutron intensity due only to the magnetic scattering at various temperatures is shown in Fig. 2 for the (111), (200), and (220) reflections. The magnetic

* This work was performed under the auspices of the U. S. Atomic Energy Commission.
[1] B. T. Matthias, R. M. Bozorth, and J. H. Van Vleck, Phys. Rev. Letters **7**, 160 (1961).
[2] C. Olsen, N. Nereson, and G. Arnold, Suppl. J. Appl. Phys. **33**, 1135 (1962).
[3] H. A. Eich, N. C. Baenziger, and L. Eyring, J. Am. Chem. Soc., **78**, 5147 (1956).
[4] C. S. Barrett, Brit. J. Appl. Phys. **7**, 426 (1956).

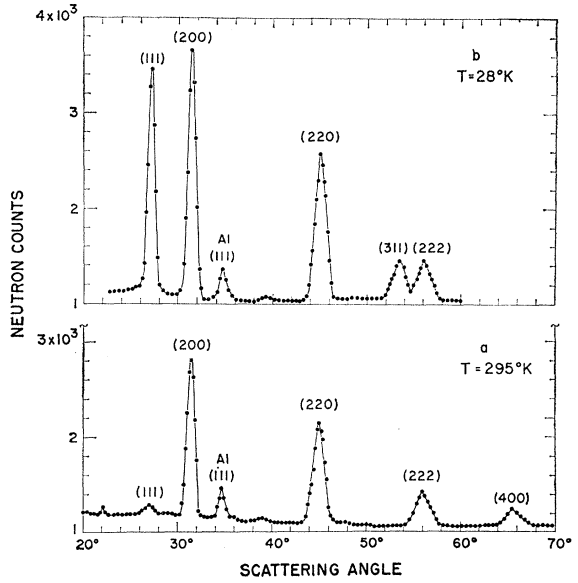

FIG. 1. Neutron diffraction results obtained from EuO powder, (a) at room temperature and (b) at 28°K. The aluminum peak at 34.5° originates from the cryostat container.

component was obtained by subtracting the nuclear scattering component for each reflection from the total intensity. All of the above reflections exhibit intensity variations with temperature which agree with the square of a Brillouin function having a spin of 7/2 and a Curie temperature of 77°K. The calculated Brillouin function was normalized to the experimental data over the 20 to 30°K temperature range.

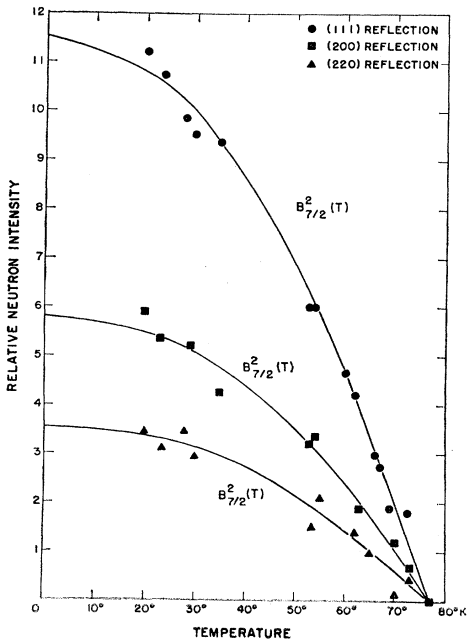

FIG. 2. Neutron intensity vs temperature for magnetic scattering from various EuO planes. The solid lines are squared Brillouin functions calculated for a Curie temperature of 77°K and a spin quantum number of 7/2.

The above results indicate that the magnetic behavior of Eu^{2+} with respect to temperature is somewhat different in EuO than in the metal Eu, where it has been assumed that Eu exists as Eu^{2+}. Experiments[2] on Eu metal foil have shown that the neutron intensity from magnetic scattering varies as $(T_N-T)^{\frac{1}{2}}$. The reasons for this difference in behavior are not understood at the present time.

The present diffraction data from the EuO powder sample cannot be used to determine the direction of the magnetic moment relative to the crystallographic axes. This is due to the fact that q^2 in the expression for the resultant intensity structure factor,[5] $F^2=F_{\text{nuc}}{}^2+q^2F_{\text{mag}}{}^2$, is equal to 2/3 irrespective of the assumed moment alignment direction. However, the magnetic contribution to the diffraction peaks can be effectively employed to establish a section of the magnetic amplitude form factor curve for Eu^{2+}. In order to accomplish this objective, the calculated Brillouin curves in Fig. 2 have been used to evaluate the saturation value of the neutron intensity due to magnetic scattering at 0°K. These saturation intensity values together with other information concerning the magnetic reflecting planes are given in Table I. The absolute intensities of $F_{\text{mag}}{}^2$, as calculated in Table I, are based upon Ni powder as a calibrating standard.

The magnetic intensity structure factor can be expressed as[5]

$$F_{\text{mag}}{}^2=(4p)^2\exp(-2W)=4.65\times10^{-24}S^2f^2\times\exp(-2W)\text{ cm}^2, \quad (1)$$

where $p=0.539\times10^{-12}\ Sf$ cm, S is the effective spin quantum number, f is the magnetic amplitude form factor, and $\exp(-2W)$ is the Debye temperature correction factor. Since the Eu^{2+} ion is in an ^8S state,[1] the orbital angular momentum is zero and $S=7/2$. Therefore, Eq. (1) becomes

$$F_{\text{mag}}{}^2=56.9\times10^{-24}f^2\exp(-2W)\text{ cm}^2, \quad (2)$$

and f^2 can be calculated from the experimental values of $F_{\text{mag}}{}^2$ if the temperature factor is known. It is difficult to accurately determine the magnetic temperature factor of EuO since the characteristic temperature is not known, and the masses of the atoms are widely different. However, the temperature factor can be evaluated for the nuclear scattering data from the slope of the straight line in Fig. 4.

Since the magnetic scattering data in Table I are referred to 0°K, the magnetic temperature factor is estimated to be 1/2 to 1/3 that for the nuclear data. If the characteristic temperature is greater for the magnetic reflections than for the nuclear reflections, the temperature factor correction would be even less than the

[5] G. E. Bacon, *Neutron Diffraction* (Oxford University Press, New York, 1955).

TABLE I. Calculated values of F_{mag}^2 and f derived from magnetic scattering data of EuO.

hkl	Scattering angle, 2θ[a]	$(\sin\theta)/\lambda$ (10^8 cm^{-1})	$P_{hkl(mag)}$[b]	Multiplicity, j	$F_{hkl(mag)}^2$[c] (10^{-24} cm^2)	f[d]
(111)	27.10°	0.170	2400±150	8	27.7±2	0.70±0.05
(200)	31.38°	0.195	1200±80	6	24.6±2	0.66±0.05
(220)	44.94°	0.274	740±50	12	15.2±1	0.52±0.04
(311)	53.30°	0.322	750±70	24	10.6±1	0.43±0.03

[a] The scattering angle was calculated for a EuO lattice spacing of $a_0=5.144$ Å.
[b] The quantity, $P_{hkl(mag)}$ is proportional to the neutron intensity observed from only magnetic scattering at $T=0$°K.
[c] $F_{hkl(mag)}^2$ is the intensity structure factor for magnetic scattering (including the Debye temperature correction factor) and is calculated from the usual expression,[5] $P_{hkl(mag)}=Kp't\exp(-\mu t\sec\theta)j_{hkl}N_c^2q^2F_{hkl(mag)}^2/\rho\sin^2 2\theta$. The constant, $K=18.55\times10^{-18}$, was obtained from the Ni powder standard.
[d] The magnetic amplitude form factor, f, has not been corrected for variation of the Debye temperature factor with scattering angle.

above estimate. Using the maximum estimated temperature correction results in increasing the value of f by only 5% for the (311) reflection; the other reflections would have even smaller corrections. Since the temperature corrections are less than the experimental errors in f, no correction has been applied to the values of f computed in Table I.

The experimental values of f for Eu^{2+} vs $(\sin\theta)/\lambda$ are plotted in Fig. 3. Also shown is a curve calculated by Blume, Freeman, and Watson[6] for the Eu^{2+} ion. The experimental results and calculated curve differ in absolute magnitude by about 20%, but the agreement between the relative shape or slope of the curve is very good. The experimental data show that the angular form factor f falls to half-value at $(\sin\theta)/\lambda=0.29$, whereas the calculated curve indicates a half-value point of $(\sin\theta)/\lambda=0.34$. A value of g different from 2 for Eu^{2+} would influence the above results.

It is of interest to speculate on what type of mechanism may be responsible for the ferromagnetism in EuO. The compound EuO is isostructural with MnO, MnS, MnSe, and CoO which are antiferromagnetic and whose properties are explainable in terms of a superexchange mechanism[7,8] through the intervening oxygen atoms. It appears that some modification may be necessary in the superexchange theory to explain these differences in behavior.

TABLE II. Calculated values of F_{nuc}^2 derived from nuclear scattering data of EuO.

hkl	Scattering angle, 2θ[a]	$(\sin^2\theta)/\lambda^2$ (10^{16} cm^{-2})	$P_{hkl(nuc)}$[b]	Multiplicity, j	$F_{hkl(nuc)}^2$[c] (10^{-24} cm^2)
(200)	31.38°	0.0378	1580±100	6	21.6±1.4
(220)	44.94°	0.0755	1560±70	12	21.3±1.1
(222)	55.84°	0.1132	625±40	8	19.3±1.3
(400)	65.51°	0.1512	350±40	6	19.6±2.5

[a] The scattering angle was calculated for a EuO lattice spacing of $a_0=5.144$ Å.
[b] The quantity, $P_{hkl(nuc)}$, is proportional to the neutron intensity observed for the various diffraction peaks at a temperature of approximately 80°K.
[c] $F_{hkl(nuc)}^2$ is the intensity structure factor for nuclear scattering (including the Debye temperature correction factor) and is calculated from the usual expression,[5] $P_{hkl(nuc)}=Kp't\exp(-\mu t\sec\theta)j_{hkl}N_c^2F_{hkl(nuc)}^2/\rho\sin^2 2\theta$.

[6] A. J. Freeman (private communication).
[7] H. A. Kramers, Physica **1**, 182 (1934).
[8] P. W. Anderson, Phys. Rev. **79**, 350, 705 (1950).

Nuclear Scattering of EuO

The nuclear contribution to the diffraction peaks of EuO can be utilized to determine the neutron coherent scattering amplitude of Eu. This amplitude has been previously determined from Eu_2O_3[9]; however, the present value is more accurate since the evaluation is based upon three diffraction peaks instead of only one peak as in the case of the first determination. Several diffraction survey runs on the EuO sample were made at temperatures above the transition temperature (about 80°K) in order to accurately establish the nuclear intensities of the diffraction peaks. The procedure for calculating the Eu scattering amplitude follows the method of Shull and Wollan.[10] Nickel powder, for which the scattering amplitude $f_{coh}=1.05\times10^{-12}$ cm, was again used as a calibrating standard.

Data on the nuclear diffraction peak intensities and the calculation of F_{nuc}^2, the effective intensity structure factor, for the various diffraction peaks are given in Table II. The evaluation of F_{nuc}^2 at 0° scattering angle was determined by the usual method[10] of graphing F_{nuc}^2 on a logarithmic scale vs $(\sin^2\theta)/\lambda^2$ and extrapolating the straight line back to 0° (see Fig. 4). The data for

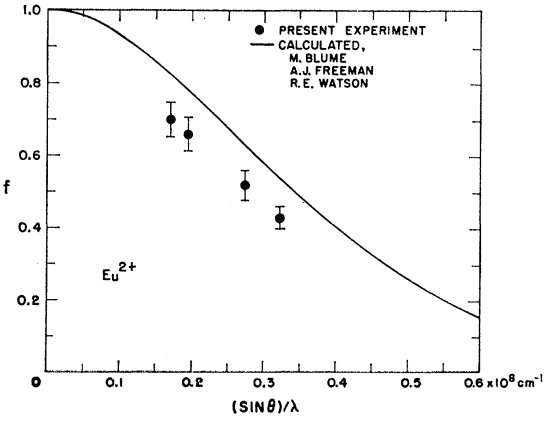

FIG. 3. Variation of the magnetic amplitude form factor for the Eu^{2+} ion with $(\sin\theta)/\lambda$. The experimental values have not been corrected for the Debye temperature factor.

[9] G. Arnold and N. Nereson, Phys. Rev. **124**, 1848 (1961).
[10] C. G. Shull and E. O. Wollan, Phys. Rev. **81**, 527 (1951).

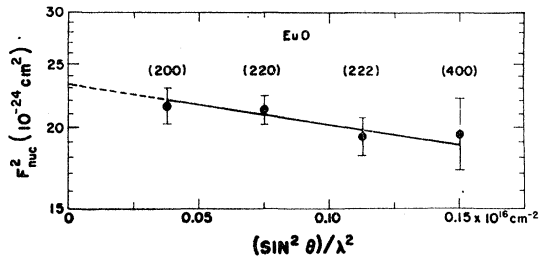

FIG. 4. Graphical method for determining F_{nuc}^2 at 0° scattering angle.

the (200), (220), and (222) diffraction peaks are the most reliable and the straight line is justified from these data; the error associated with the (400) peak is large due to the small neutron intensity observed from this reflection. The data in Fig. 4 give a value of $F_{\text{nuc}}^2=23.4\pm1.5\times10^{-24}$ cm^2 at an angle of 0°.

The diffraction peaks utilized here are from EuO reflection planes having even indices. Therefore, $F_{\text{nuc}}^2=16(f_0+f_{\text{Eu}})^2\exp(-2W)$, where $\exp(-2W)$ is the Debye temperature correction factor; at an angle of 0°, $F_{\text{nuc}}^2=16(f_0+f_{\text{Eu}})^2=23.4\times10^{-24}$ cm^2. Since Eu has resonances near the neutron wavelength used (1.391 Å), the expression for the scattering amplitude must be expressed in complex form[11] as $f_{\text{Eu}}=f_0(\text{Eu})+\Delta f'+i\Delta f''$. The constants $\Delta f'$ and $\Delta f''$ have been evaluated previously[9] as $\Delta f'=-0.248$ and $\Delta f''=-0.024$. Taking $f_0=0.58\times10^{-12}$ cm, one obtains $f_0(\text{Eu})=(0.88\pm0.04)\times10^{-12}$ cm for the nonresonant coherent scattering length and $|f_{\text{Eu}}|=(0.63\pm0.03)\times10^{-12}$ cm for the absolute value of the coherent scattering length. In the case of the present neutron wavelength, the imaginary term in the complex expression for f_{Eu} is quite small and therefore $f_{\text{Eu}}\cong f_0(\text{Eu})+\Delta f'\cong|f_{\text{Eu}}|$.

[11] S. W. Peterson and H. G. Smith, Phys. Rev. Letters **6**, 7 (1961).

Since the previous result on the Eu coherent scattering length was published, an error in the Eu_2O_3 sample transmission has been discovered. When the former data are corrected for this transmission error, the earlier experiment gives values of $f_0(\text{Eu})=(0.85\pm0.05)\times10^{-12}$ cm and $|f_{\text{Eu}}|=(0.60\pm0.04)\times10^{-12}$ cm at 1.391 Å. The results from the two experiments are in agreement within the quoted experimental errors.

There is a small nuclear peak present at the (111) reflection position [see Fig. 1(a)]; the intensity of this nuclear peak is proportional to $(f_{\text{Eu}}-f_0)^2$. The data from this peak were unsatisfactory for a calculation of f_{Eu} on account of (1) the large statistical error due to the small neutron intensity, and (2) the uncertainty of the contribution to the intensity of second-order neutrons from the (222) reflection. An approximate calculation and a substantiating experiment showed that the intensity of the (111) reflection is four to five times larger than the second-order contribution from the (222) reflection. Therefore, the presence of the (111) peak indicates that the scattering amplitude of europium is slightly larger or smaller than that of oxygen; the other diffraction peak data confirm that $|f_{\text{Eu}}|-f_0>0$.

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