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Paramagnetic Scattering of Neutrons by Rare Earth Oxides

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The magnitude and angular dependence of the paramagnetic scattering of neutrons has been studied for the trivalent ions in the rare earth oxides, Pr_2O_3, Nd_2O_3, and Er_2O_3. These rare earth ions have large angular momentum contributions to their magnetic moments and one object of the investigation was to obtain a better understanding of the magnetic scattering in such cases. The angular distribution of the scattering for samples at room temperature is compared with the theoretical results of Trammell which are given in the following paper. The calculations based on screened hydrogenic wave functions give results in reasonably good accord with the measurements when the screening constant is taken as an adjustable parameter which is then determined, within limits, by the data. Scattering measurements were also made at liquid nitrogen and liquid hydrogen temperatures, and within a few percent no changes and, hence, no crystalline field or exchange effects were observed.

INTRODUCTION

INVESTIGATIONS of the magnetic scattering of neutrons,[1] which have been carried out thus far, have been concerned, primarily, with the ions or metals of the 3*d* transition group in which the orbital contributions to the moments are wholly or partially quenched by crystalline field interactions. In the present work, the neutron technique is applied to ions of the rare earth series, in which the magnetic moments arise from the unfilled 4*f* shell in which the electrons are more deeply buried within the atom than the 3*d* electrons of the iron group, and they are thus less affected by crystalline fields. Susceptibility measurements on a variety of rare earth salts give effective magnetic moments at near room temperature which correspond closely to the values to be expected for the free ions, the orbital contributions being thus wholly operative.

The theory for the magnetic scattering of neutrons as developed by Bloch,[2] Schwinger,[3] Halpern and Johnson,[4] and others, has been limited, in the consideration of the angular dependence of the scattering, to the case of ions having spin moments only. As a consequence of the present studies on the rare earths, G. Trammell of this laboratory was led to extend the application of the theory to include the more general situation involving both spin and orbital contributions to the magnetic moments. This work appears in the following paper.[5] This problem has now also been considered by Kleiner.[6]

Only a few of the rare earths can, at the moment, be studied by the neutron-scattering technique, either because they are not available in sufficient quantities, or because in several cases they possess a prohibitively large capture cross section. Fortunately, the development of the ion exchange method in recent years has made some of them available in useable amounts. The magnetic scattering studies reported here are primarily concerned with the sesquioxides of neodymium and erbium, and in some of these measurements, separated isotopes of neodymium have been used. Some measurements are also reported for Pr_2O_3.[7] Neodymium and erbium constitute an interesting pair in that their trivalent ions have, in the ground state, the same spin and angular momentum ($L=6$, $S=3/2$). Nd^{+++} has three 4*f* electrons and according to Hund's rule the normal state is ${}^4J_{9/2}$ and Er^{+++} has three vacancies in the 4*f* shell corresponding to the state ${}^4J_{15/2}$. There is Russell-Saunders coupling with L and S combining "antiparallel" and "parallel" respectively in the two ions.

The theory of the paramagnetic susceptibility of rare earth ions has been given by Hund[8] and Van Vleck.[9] In the cases of neodymium and erbium, the multiplet spacing is large compared to kT at room temperature and to a close approximation only the normal state need be considered. The effective magnetic moment is then given by

$$\begin{aligned}\mu_{\mathrm{eff}}^2&=\beta^2\left[\mathbf{L}\cdot\frac{\mathbf{J}}{|\mathbf{J}|}+2\mathbf{S}\cdot\frac{\mathbf{J}}{|\mathbf{J}|}\right]^2\\&=g^2\beta^2J(J+1),\end{aligned}\tag{1}$$

where β is the Bohr magneton and g is the Landé g-factor.

Except for a term which is independent of temperature and is negligible for this case, the susceptibility

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[1] I. W. Ruderman, Phys. Rev. **76**, 1572 (1949); Shull, Strauser, and Wollan, Phys. Rev. **83**, 333 (1951); Shull, Wollan, and Koehler, Phys. Rev. **83**, 912 (1951); R. A. Erickson, Phys. Rev. **90**, 779 (1953).

[2] F. Bloch, Phys. Rev. **50**, 259 (1936); **51**, 994 (1937).

[3] J. S. Schwinger, Phys. Rev. **51**, 544 (1937).

[4] O. Halpern and M. H. Johnson, Phys. Rev. **59**, 898 (1939).

[5] G. T. Trammell, Phys. Rev. **90**, 355 (1953); Phys. Rev. (to be published).

[6] W. H. Kleiner, Phys. Rev. **90**, 168 (1953).

[7] We are indebted to Dr. F. H. Spedding of Ames Laboratory for the praseodymium and neodymium samples and to Dr. G. E. Boyd of the Oak Ridge National Laboratory Chemistry Division for the erbium sample. The separated isotopes were obtained from the Stable Isotopes Division of Oak Ridge National Laboratory.

[8] F. Hund, Z. Physik **33**, 855 (1925).

[9] J. H. Van Vleck, *The Theory of Electron and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

for a free ion is related to μ_{eff} by

$$\chi = N\mu_{\mathrm{eff}}^2/3kT. \tag{2}$$

For the rare earth oxides considered here the susceptibility has, however, been shown to follow the Curie-Weiss law over a wide range of temperature:[10–12]

$$\chi = C/(T+\Delta), \tag{3}$$

with Weiss constants Δ in the range from 10° to 50°. This indicates that there is in these compounds some effect of exchange or of crystalline field splitting or both.

Evidence for crystalline field effects has been obtained at low temperatures by Gorter and deHaas,[13] Spedding,[14] Van den Handel,[15] and Bleaney and Scovil[16] for various dilute salts of the rare earths and these experimental results have served as the basis for the theoretical calculations of Penney and Schlapp,[17] Spedding,[14] and Elliot and Stevens.[18] Presumably, similar effects should also be expected in the magnetically more concentrated oxides. Selwood[11] has investigated the effect on the Weiss constant of dilution of Nd_2O_3 with La_2O_3 and he concludes that an appreciable fraction of the Weiss constant for Nd_2O_3 may be attributed to exchange interactions. A direct measurement of the g-value for Nd_2O_3 has been carried out by Sucksmith[19] which is in good agreement with the Hund value for Nd^{+++}. This measurement, then, indicates that the effective moment at not too low temperatures is that of the free ion.

The differential cross section for the scattering of slow neutrons by a free paramagnetic ion depends also on the effective magnetic moment of the ion. There is an angular dependence of the magnetic scattering arising from the spacial distribution of the spin and orbital currents in the atom and this aspect of the problem, with which this work is primarily concerned, will be discussed in the last section of the paper. For long wavelength neutrons or for scattering in the near forward direction, the differential cross section for a free paramagnetic ion with Russell-Saunders coupling has been shown to be[3,5]

$$\sigma(k)_{k\to 0} = \frac{2}{3}\left(\frac{e^2\gamma}{2mc^2}\right)^2 g^2J(J+1), \tag{4}$$

where $k = (4\pi/\lambda)\sin(\varphi/2)$, in which λ is the wavelength and φ the scattering angle; γ is the magnetic moment of the neutron in nuclear Bohr magnetons, and $g^2J(J+1)$ is the effective magnetic moment of the free ion in Bohr magnetons.

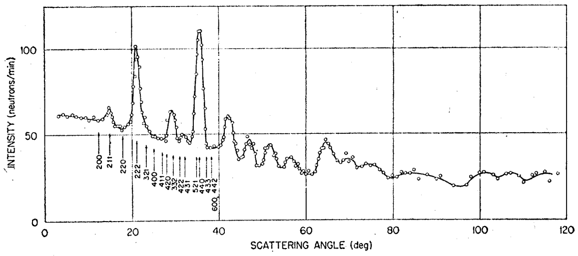

FIG. 1. Diffraction pattern for erbium oxide (Er_2O_3).

DISCUSSION OF SAMPLES

The samples were all ignited to remove any possible contamination with water and CO_2, and were stored in a desiccator until used. In every case, x-ray diffraction patterns were made to establish the crystallographic form of the materials. The diffraction cells were sealed, and weighed before and after each run. In some cases special procedures were followed and these are described for the individual samples below.

The Nd_2O_3 sample was obtained and used first in the hexagonal form. It was of high purity as determined spectroscopically at Ames, and also by C. Feldman of Oak Ridge National Laboratory. The thermal capture cross section was measured by H. Pomerance and found to have a value of 42 barns. The magnetic susceptibility was measured over the temperature range of 80°K to 300°K, by C. Nelson of this laboratory, and the results of these measurements gave a Weiss constant of $27° \pm 7°$ and an effective magnetic moment of 3.8 ± 0.1 Bohr magneton.

For the measurements on the cubic form of Nd_2O_3 the sample was converted by the method of Löhberg.[20] Complete conversion was shown by an x-ray pattern as well as by the neutron pattern.

The praseodymium sample was received in the form of the black oxide, Pr_6O_{11}. The pale green sesquioxide was prepared by reducing Pr_6O_{11} in a hydrogen atmosphere at 700°C. After the reduction was complete, the sample was held at 400°C for six hours in a vacuum. Measurements of the magnetic susceptibility of this preparation were also made.

MEASUREMENTS

Erbium Oxide

The room temperature diffraction pattern of Er_2O_3 taken at a neutron wavelength of 1.16A is shown in Fig. 1. The Bragg reflections are due entirely to coherent nuclear scattering and the coherent cross section for erbium as evaluated from patterns of this type is $\sigma_{\mathrm{coh}} = 7.8 \pm 0.4$ barns. In addition to the coherent contribution, there is also a considerable amount of

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[10] S. Rabideau, J. Chem. Phys. **19**, 874 (1951).
[11] P. W. Selwood, J. Am. Chem. Soc. **55**, 3161 (1933).
[12] B. Cabrera and A. Duperier, Comptes rend. **188**, 1640 (1929).
[13] C. J. Gorter and W. T. de Haas, Leiden Comm. 218b (1931).
[14] F. H. Spedding, J. Chem. Phys. **5**, 316 (1937).
[15] J. Van den Handel, Thesis, Leiden, 1942 (unpublished).
[16] B. Bleaney and H. E. D. Scovil, Proc. Phys. Soc. (London) **A63**, 1369 (1950); **64**, 204 (1951).
[17] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932).
[18] R. J. Elliot and K. W. H. Stevens, Proc. Phys. Soc. (London) **A64**, 205 (1951); Proc. Roy. Soc. (London) **A215**, 437 (1952).
[19] W. Sucksmith, Proc. Roy. Soc. (London) **A135**, 276 (1932).
[20] K. Löhberg, Z. physik. Chem. (B) **28**, 402 (1935).

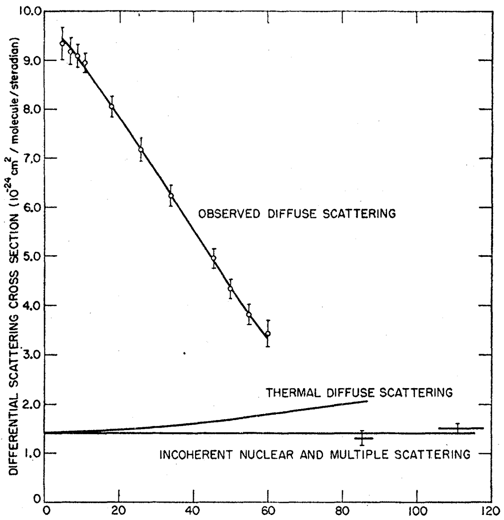

FIG. 2. Diffuse scattering by Er_2O_3. The magnetic scattering is represented by the difference between the measured curve and the other indicated contributions.

diffuse scattering arising from the presence of several isotopes in erbium and from thermal and multiple scattering effects. The decrease of the diffuse scattering with increasing angle arises from the paramagnetic scattering which predominates at small angles. The determination of both the magnitude and the angular dependence of the paramagnetic scattering requires the evaluation of the other contributions to the total scattering.

The measured total diffuse scattering standardized against the coherent scattering by nickel ($\sigma_{\mathrm{coh}}^{\mathrm{Ni}}=13.4 \pm 0.2$ barns) is shown by the upper curve in Fig. 2. The curve cannot be directly determined to scattering angles greater than 60° because it is then impossible to distinguish the diffuse background from the unresolved Bragg peaks. The accuracy of the measurements in the first half of the pattern is determined, primarily, by counting statistics and by the reliability of the nickel cross section used in the standardization and at scattering angles below 10° by an appreciable background arising from close proximity to the incident beam. In the region from 40° to 60°, the errors are increased by the lack of complete resolution of the Bragg peaks.

To determine what part of the total scattering is of paramagnetic origin, an evaluation must now be made of the other contributions to the diffuse scattering.

The multiple scattering for this case is small, because thin sample geometry was required by the small amount of material available and because of the large thermal capture cross section of erbium. Since this scattering has, if any, only a small dependence on angle it can be included with the other isotropic components.

The total nuclear-scattering cross section per molecule ($2\sigma_{\mathrm{Er}}+3\sigma_{\mathrm{O}}$) can best be determined in the present experiment from the scattering data at large angles, where the paramagnetic scattering can be assumed to be negligible. If it is assumed that the interference effects over the large angle region average out, as suggested by the high density of lines in this region, then the resulting total cross section can be obtained from the average scattering in this large-angle region. The isotropic background level arising from the spin and isotope effects, and to a small extent from multiple scattering, can then be evaluated by subtracting from the total scattering the average coherent scattering obtained from the known cross sections of erbium and oxygen. The background level was also evaluated by direct calculation of the intensity of the twenty-five reflections which make up the coherent part of the scattering in a five degree interval at eighty-five degrees. The value for the angularly independent scattering thus obtained is shown in Fig. 2 by the horizontal line drawn through the average of the two experimental points.

The expected thermal scattering is illustrated in Fig. 2 also, and this is based upon the temperature factor, $2w=1.0$, which was suggested by the analysis of the coherent intensities in the compounds, Er_2O_3 and cubic Nd_2O_3, of this investigation and in the isomorphous compound, Sc_2O_3, studied by Milligan *et al.*[21]

The paramagnetic scattering can now be obtained by subtracting from the total diffuse-scattering curve the contributions arising from incoherent nuclear and multiple scattering and from the thermal effect.

The results thus obtained, expressed as differential cross sections per erbium ion, are shown by the points with their respective uncertainties in Fig. 3. The para-

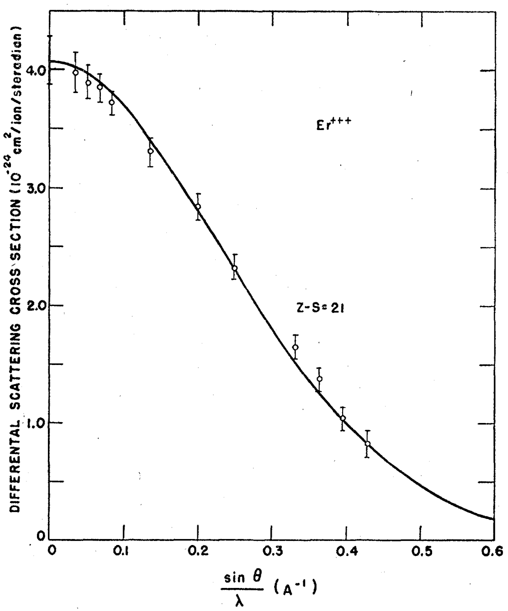

FIG. 3. Paramagnetic-scattering cross section per erbium ion in Er_2O_3.

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[21] Milligan, Vernon, Levy, and Peterson, J. Phys. Chem. (to be published).

magnetic cross section in the forward direction obtained by a reasonable extrapolation of the data gives 4.1 barns per unit solid angle per erbium ion. This corresponds to an effective magnetic moment of 9.2 Bohr magnetons whereas the value for a free ion is 9.6 Bohr magnetons. If this can be considered as a real difference, it would indicate a possible small effect arising from crystalline fields. The fact that susceptibility measurements give a moment which agrees with the free ion value, does not necessarily rule out the lower value for the neutron measurements because field splitting can give rise to inelastic processes in neutron scattering. The fact that there is no observable change of the forward scattering with temperature (see later section) does, however, favor the free ion assumption for neutron scattering also. Much of the uncertainty in the forward scattering must be ascribed to the measurements of the isotropic scattering level. It is felt that apart from some unknown sources of error, the uncertainties in the forward scattering can be represented by the indicated error line, which does not quite include the 4.4 barn value which would correspond to a moment of 9.6 Bohr magnetons.

Discussion of this point in its relation to the angular dependence of the scattering, and the comparison of the data with the theoretical results of Trammell, will be given in the last section following the presentation of the other measurements.

Neodymium Oxide

A neutron diffraction pattern of hexagonal neodymium oxide taken in cylindrical cell geometry at room temperature with 1.16A neutrons is shown in Fig. 4. The several components of the scattering in this pattern are those enumerated in the preceding section which dealt with Er_2O_3, but the distribution of intensities among the components is quite different in the two cases.

The diffuse scattering is relatively high, but its angular dependence is not nearly as pronounced as in the preceding case. The calculated magnitude of the magnetic-scattering cross section in the forward direction for Nd^{+++} is smaller by a factor of about seven than that for Er^{+++}, so that an appreciable part of the diffuse scattering in the forward direction must be attributed to incoherent nuclear scattering and multiple scattering.

In measuring the total diffuse scattering, several patterns of the hexagonal neodymium oxide were taken under experimental conditions designed to favor the study of a particular component of the diffuse scattering, or a particular angular region of the pattern. The whole region was studied with cylindrical cell geometry and then to enhance the scattered intensities in the low scattering angle region (5° to 40°), in which resolution can be sacrificed, a thick sample in flat cell geometry was studied.

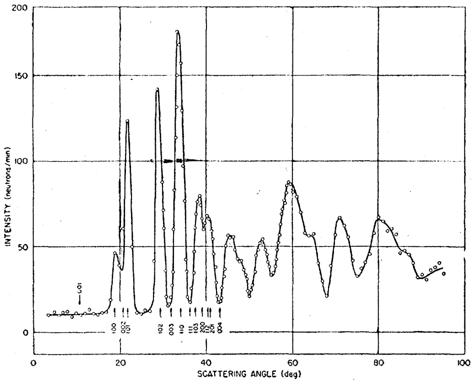

FIG. 4. Diffraction pattern for neodymium oxide (Nd_2O_3 hexagonal form).

The total measured scattering in the near forward direction was found to be somewhat greater than twice that to be expected from magnetic scattering alone. Since much of the diffuse scattering must, then, be ascribed to isotopic incoherent and multiple scattering, the procedure which was used for evaluating these contributions in the case of erbium, where they represented a relatively small part of the total, would be quite unsatisfactory for neodymium.

In view of this, another approach was made to the problem through the study of the diffuse scattering from isotopically enriched samples. Three samples of neodymium oxide enriched in Nd^{142}, Nd^{144}, and Nd^{146} were investigated, and for these samples the situation with respect to nuclear cross sections is much more favorable than for the normal isotopic mixture. The magnetic scattering, arising from the atomic electrons, should remain unchanged.

The three samples were enriched to about ninety-five percent and since their main constituents are all even-even isotopes, the incoherent nuclear scattering may be expected to be markedly reduced from that of normal neodymium. The capture cross sections for the three enriched samples were measured by Pomerance[22] and they were found to be much smaller than for normal neodymium. Thus the correction of transmission data for capture could be expected to yield reliable total scattering cross sections. The coherent scattering cross sections for the three isotopic samples were measured from the coherent reflections in the patterns.[23]

Thin sample geometry was chosen for the two purposes of minimizing multiple scattering and for making optimum use of the small quantities of isotopically enriched material available. As a consequence, the scattered intensities were low and the diffuse scattering analysis was confined to the near forward direction where the magnetic scattering is a maximum.

In each case, for the particular geometry employed, a good estimate for multiple scattering could be made.

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[22] H. Pomerance, Phys. Rev. **88**, 412 (1952).

[23] W. C. Koehler and E. O. Wollan, Phys. Rev. **91**, 596 (1953).

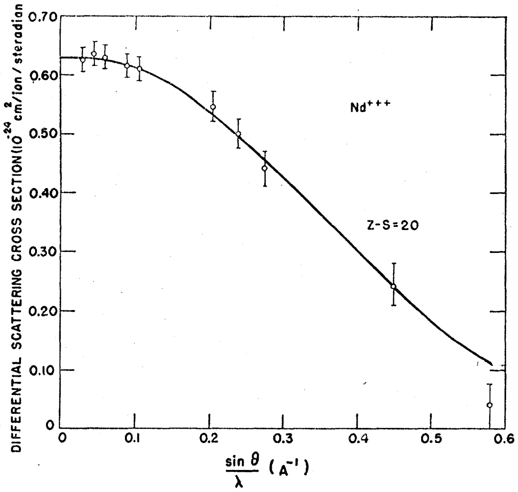

FIG. 5. Paramagnetic-scattering cross section per neodymium ion in Nd_2O_3. The forward scattering has been taken as that for the free ion.

The incoherent nuclear contribution was calculated from the measured total and coherent scattering cross sections. In the forward direction, the thermal scattering is negligible, so that the observed forward diffuse scattering must be due to the two effects mentioned above and to paramagnetic scattering. The difference between the total observed scattering and the contribution from incoherent nuclear and multiple scattering for each sample should correspond to the paramagnetic scattering.

The forward magnetic-scattering cross section, which resulted when the average of the three determinations was taken, is 1.33±0.10 b/steradian molecule and the corresponding magnetic moment per neodymium ion is 3.7 Bohr magnetons. The theoretical effective moment calculated for neodymium ion in the state ${}^4J_{9/2}$ is 3.62 Bohr magnetons. The estimated uncertainty in the forward magnetic cross section is, thus, plus or minus seven percent corresponding to a plus or minus 3.5 percent uncertainty in the magnetic moment. Within this uncertainty, the effective magnetic moment as measured here agrees with the calculated value.

Once the forward magnetic scattering for the neodymium ion had been established, the analysis of the diffuse-scattering data of the normal neodymium samples could be made. The isotropic scattering level in the patterns was then obtained and the angularly dependent scattering as measured from this base line is composed of paramagnetic scattering and thermal scattering, for which correction can be made on the same basis as previously described for Er_2O_3. The angular dependence of the paramagnetic scattering can then be directly determined over the angular region in which the coherent peaks are reasonably well resolved. The results thus obtained are shown in Fig. 5. At scattering angles greater than 60°, where the peaks are not resolved, some information about the angular dependence of the scattering can be obtained by comparing the diffraction pattern of Nd_2O_3, Fig. 4, with that of the isomorphous and diamagnetic La_2O_3 shown in Fig. 6. This pattern is characterized by a rising trend in the large angle region which is caused by the lack of resolution among the coherent peaks and to the angular dependence of the thermal diffuse scattering. It is apparent from an inspection of the two patterns that in Nd_2O_3 the upward trend is compensated by the angular behavior of the magnetic scattering.

In order to extend the range of the observed magnetic-scattering curve for Nd_2O_3, an attempt was made to place the comparison of the two patterns on a quantitative basis. Structure factors for the two compounds were calculated for all observable reflections and the intensities to be expected for a few convenient angular intervals were computed, and these computed intensities together with the expected thermal-scattered intensities were used to estimate the background scattering in the two patterns. For the case of La_2O_3, where no magnetic scattering is to be expected, this procedure should lead to an isotropic background identical with that observed at small scattering angles. The results of these calculations did reproduce the observed forward scattering to twenty-five percent and with this sensitivity the corresponding calculation was made for Nd_2O_3 at large angles.

The points so obtained are also shown in Fig. 5. These points are of rather low precision but they indicate the behavior of the magnetic-scattering curve at those angles for which a more accurate determination cannot be made.

Praseodymium Oxide

The magnetic scattering from Pr_2O_3 was also investigated. The nuclear scattering and capture cross sections for Pr are known[23,24] and their magnitudes relative to the magnetic-scattering cross section are such that the forward magnetic-scattering cross section could be determined by the method described for the isotopic neodymium samples. For example, in the thin sample run on this oxide, the contributions from the incoherent nuclear scattering and from multiple scattering amounted to twenty-three percent of the total

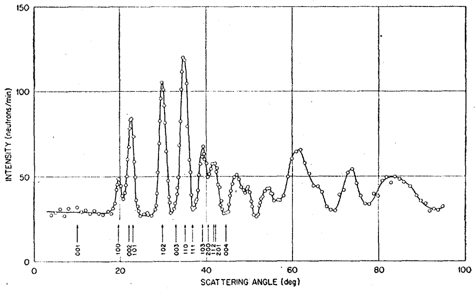

FIG. 6. Diffraction pattern for lanthanum oxide (La_2O_3).

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[24] H. Pomerance, Phys. Rev. **83**, 641 (1951).

observed forward scattering. The magnetic differential scattering cross section per praseodymium ion obtained from the analysis of the data was 0.67 b/steradian as compared to the calculated value of 0.617 b/steradian.

The angular dependence of the magnetic scattering from Pr_2O_3 was determined in the manner described in the preceding section, but due to an accidental exposure of the sample to the atmosphere the data for very large angles were invalid and the magnetic scattering was obtained only for $\sin\theta/\lambda$ less than 0.3. The data accumulated over this range were, however, sufficiently extensive to demonstrate the essential features of the magnetic scattering, and the large-angle measurements were not repeated. Within the precision of the experiment, the magnetic-scattering cross section of Pr for $\sin\theta/\lambda$ less than 0.3 was scarcely distinguishable from the magnetic-scattering cross section of Nd over the same range.

That the magnetic scattering from these two ions is similar is, perhaps, not too surprising. Trivalent praseodymium is in a $^3H_4$ spectroscopic ground state and the magnetic moment calculated for this configuration is 3.58 Bohr magnetons. For Nd^{+++}, in a $^4J_{9/2}$ state, the moment is 3.62 Bohr magnetons and the calculated magnetic differential scattering cross sections for the forward direction differ, in the two cases, by slightly more than two percent.

In the praseodymium ion the cancellation of the orbital contribution to the scattering by the spin contribution is comparable to that in the neodymium ion and the resultant form factors may be expected to be quite similar. Detailed calculations for this case have not been made, but the approximate model discussed below for Nd^{+++} and Er^{+++} would predict the same general features in the angular dependence of the scattering by praseodymium ion as by neodymium ion.

Cubic Neodymium Oxide

The neutron diffraction pattern of cubic neodymium oxide, which was studied in an attempt to refine the parameters of the cubic structure, was also analyzed with respect to diffuse scattering. The analysis of the data gave results which agreed, within the experimental errors, with those for the hexagonal structure.

Low Temperature Measurements

A set of measurements on the oxides of Pr, Nd, and Er was obtained at the temperatures of liquid nitrogen and liquid hydrogen. For comparison purposes a room temperature run with the sample in the cryostat was also made. Slight changes in the coherent and diffuse scattering at the different temperatures from the several samples were observed which could be attributed to changes in the thermal effect on the scattering and to the change of sample geometry with decreasing temperature. Within the experimental uncertainties of about five percent, the magnetic scattering in the near forward direction was found to be the same at 21°K as at room temperature. There is thus no evidence for a crystalline field effect from the low-temperature measurements.

COMPARISON OF Nd^{+++} AND Er^{+++} RESULTS WITH THEORY

As we have mentioned, the derivation of the cross-section formula for magnetic scattering of neutrons by free magnetic ions as carried out by Halpern and Johnson for the case of spin only, has been extended by G. Trammell, in the following paper, to the case where there are both orbital and spin contributions in Russell-Saunders coupling and the multiplet separation is sufficiently great so that only the ground state is involved.

For the case of paramagnetic ions with no crystalline field effects, Trammell gives the cross section in the form

$$\sigma(k)d\Omega=\left(\frac{e^2\gamma}{2mc^2}\right)^2\sum_{\nu=0}^{l}\left[G_{2\nu,\,2\nu+1}{}^{L}F_{2\nu}{}^{2}(k)-G_{2\nu+2,\,2\nu+1}{}^{L}F_{2\nu+2}{}^{L}(k)+2G_{2\nu,\,2\nu+1}{}^{S}F_{2\nu}{}^{S}(k)+2G_{2\nu+2,\,2\nu+1}{}^{S}F_{2\nu+2}{}^{S}(k)\right]^2 d\Omega, \quad (5)$$

where the G's and F's have been evaluated in tables for the ions Er^{+++} and Nd^{+++} pertinent to the measurements reported here. He also shows that for these ions over the range of $\sin(\frac{1}{2}\varphi)/\lambda$ included in the present experiment, the cross section can be written to within five percent in the form

$$\sigma(k)=\frac{2}{3}\left(\frac{e^2\gamma}{2mc^2}\right)^2\left[L_J f_L(k)+2S_J f_S(k)\right]^2, \quad (6)$$

where $L_J\equiv\mathbf{L}\cdot\mathbf{J}/|\mathbf{J}|$ and similarly $S_J\equiv\mathbf{S}\cdot\mathbf{J}/|\mathbf{J}|$, and where the quantity $f_S(k)$ can be taken within the above mentioned accuracy as the zero-order term of the general expression and, as such, represents the spherical part in the expansion of the form factor. This quantity, then, corresponds to the form factor as defined by Pauling and Sherman[25] in terms of hydrogenic wave functions; i.e., $f_S(k)=\int\langle\rho(r,\theta,\phi)\rangle_{\text{Av}}[\sin(kr)/kr]dr$, where the average is taken over the angle variables. In the case of magnetic scattering by the rare earths, the wave functions considered are those of the unpaired $4f$ electrons which are responsible for the atomic magnetic moment.

The quantity $f_L(k)$, which has been substituted for two terms $f_0{}^L(k)+\frac{1}{2}f_2{}^L(k)$ of Trammell's paper, arises from the current distributions associated with the angular momentum of the atom. It is evident from the form of Eq. (6), and it is suggested by the treatment in the Appendix of Trammell's paper, that $f_L(k)$ can be interpreted as the Fourier transform or "form factor" of the *equivalent* spherical distribution of mag-

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[25] L. Pauling and J. Sherman, Z. Krist. 81, 1 (1932).

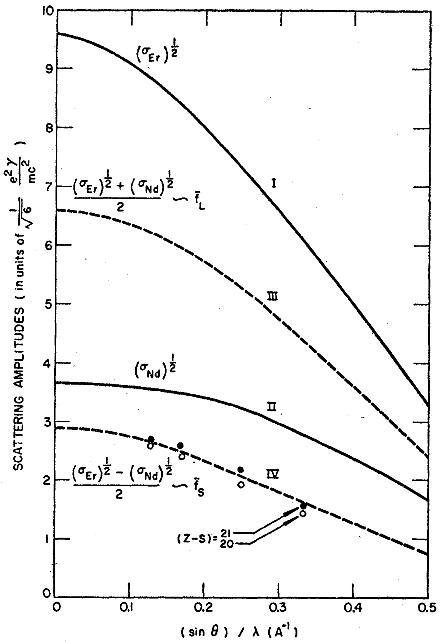

FIG. 7. Scattering amplitudes of erbium and neodymium ions, curves I and II, respectively; and the approximate resolution into average orbital and spin "form factors," curves III and IV, respectively.

netic moments, arising from the angular momentum currents, which will give the same scattering as that derived from a proper quantum mechanical averaging over the actual current distribution.

The expected magnetic scattering for Nd^{+++} and Er^{+++} can be calculated by Eq. (5) or (6) on the basis of some choice of wave function for these ions. Trammell has evaluated the scattering in terms of screened hydrogenic wave functions, and the results can be obtained from the tables given in his paper.

Although the theory applies only to free ions, we have disregarded the indication of the existence of a small crystalline field effect in Er_2O_3 and have calculated the best fitting theoretical scattering curve normalized to the measured cross section in the forward direction. This curve, calculated with $(Z-S)=21$ is shown by the solid line in Fig. 3. If the curve were to be translated upward to correspond to $\mu_{\text{eff}}=9.6$ Bohr magnetons and thus to ascribe an equivalent error to the diffuse background measurement, the best fit would be that given by Trammell with $(Z-S)=23$.

The corresponding theoretical curve for Nd^{+++} drawn for the free ion value with $(Z-S)=20$ is shown by the solid line in Fig. 5.

The screening constants given by Pauling and Sherman correspond to $(Z-S)=18$ for Nd^{+++} and 20 for Er^{+++}.

It is interesting, in connection with Eq. (6), to see how closely the effective scattering amplitudes for the erbium and neodymium ions are represented in terms of a simple interference picture involving the sum and difference of the amplitudes arising from the orbital and spin contributions. Taking the square root of both sides of Eq. (6) and evaluating L_J and $2S_J$ and disregarding the constant, one obtains

$$\begin{aligned}(\sigma_{\text{Er}})^{\frac{1}{2}} &\propto 6.40f_L+3.20f_S,\\ (\sigma_{\text{Nd}})^{\frac{1}{2}} &\propto 6.35f_L-2.73f_S.\end{aligned}\tag{7}$$

Taking the terms on the left as given by the experimental data, one can solve for the average orbital and spin magnetic "form factors" for the Er and Nd ions. The difference of the two equations is quite accurately proportional to $\bar{f}_S$ and as far as the interference picture is concerned we can take the sum as proportional to $\bar{f}_L$.

The experimental data which have now been normalized to the free-ion values are shown as curves I and II in Fig. 7. The sum and difference curves are shown as III and IV in the figure. The points on curve IV are those corresponding to screened hydrogenic wave functions with $(Z-S)$ as indicated now representing an average of the Nd and Er values. It can be seen, on close inspection that curve III falls off less rapidly with $\sin\theta/\lambda$ than curve IV. This is what would be expected from the following simple considerations. The moments associated with the spin are coincident with the electron positions, while the moments associated with the angular momentum currents are within the "orbits" and are hence located on the average closer to the center of the atom. The more compact distribution of the orbital moments gives rise to a slower fall-off of the "form factor" curve than that arising from the spin moments.

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