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Crystal Field Spectra in Rare Earth Oxides

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We have observed lines in the energy distribution of neutrons scattered by Ho_2O_3, Er_2O_3 and Tb_2O_3 corresponding to transitions within the ground state multiplet of the rare earth ion split by the crystal field. Lines were observed with energies up to 60 milli-ev and widths of the order of milli-ev. The lines have been studied at different temperatures under different conditions of neutron scattering. The results are discussed.

Introduction

In compounds of rare earths the multiplet splitting is usually large compared with the crystal field splitting. Hence the total angular momentum quantum number J is a good quantum number, and the multiplets each split into a number of levels depending on the symmetry and strength of the crystal field. For most of the rare earths at ordinary temperatures only the lowest multiplet is populated. For most compounds, probably including the oxides, the exchange interactions between the rare earth ions are considerably smaller than the interactions with the crystal field. When neutrons are magnetically scattered from the rare earth ions, the scattered neutrons go off with discrete energies corresponding to differences between the energy levels of an ion in the crystal field[1].

We have observed these crystal field splittings in the oxides, Ho_2O_3, Er_2O_3, and Tb_2O_3 (Figs. 1-3). The lines correspond to transitions between the different levels of the ground state multiplet. Analysis of the energy level diagrams is difficult. In the cubic unit cell the 32 rare earth ions occupy two kind of sites: one has point symmetry C_2 (24 atoms) and the other has symmetry C_{3i} (8 atoms). The low symmetry does not cause any reduction in the number of levels except through Kramers degeneracy. Thus Ho^{3+} (J=8) has 17 levels for site C_2 and 11 for site C_{3i}, Er^{3+} (J=15/2) has 8 levels for each site, and Tb^{3+} (J=6) has 13 levels for site C_2 and 9 for site C_{3i}. There is also, in principle, no reduction in the number of lines by symmetry; transitions in which ΔM_j=0 or $\pm$1 are possible between all levels of a given site. Thus for Ho^{3+} we expect in principle $(17\times16)+(11\times10)$ =382 lines, for Er^{3+} $2\times(8\times7)$=112 lines, and for Tb^{3+} $(13\times12)+(9\times8)$=228 lines. In fact the number of observable lines will be very much smaller, but even so it can be expected that unresolved lines will be present in the

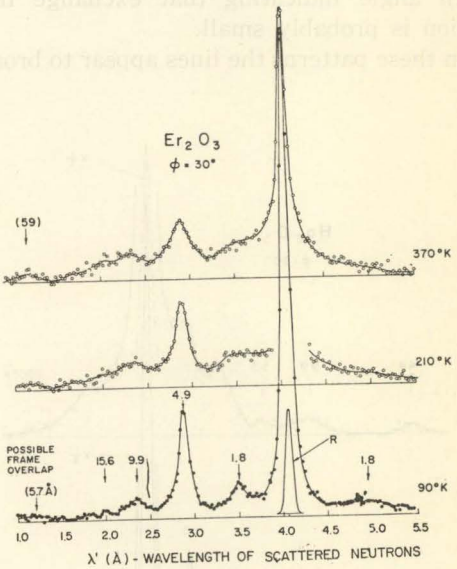

Fig. 1. Wavelength distributions of 4.059 Å neutrons scattered by Er_2O_3 at several temperatures at an angle of scattering of 30°, measured with the rotating crystal spectrometer. The ordinate scales for the three patterns are consistent. Energy transfers in milli-ev are shown. Energies in brackets indicate peaks whose existence is doubtful.

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patterns thus shifting the positions of the strongest lines, and making even more difficult the deduction of the energy levels from the results.

We have made measurements on three isomorphous oxides for which the crystal fields should be almost identical. From an assumed crystal field it should be possible to compute the three patterns. The patterns contain enough information so that agreement between theory and experiment would be convincing of the correctness of the theory.

Rotating crystal spectrometer results

Most of the experiments were carried out on the Chalk River rotating crystal spectrometer[3] with 4.059 Å neutrons, using flat specimens in transmission in the symmetric position. The results (for various temperatures) at a scattering angle (ϕ) of 30°, all corrections made, are shown in Figs. 1—3. Several more or less resolved lines are to be seen. Measurements (at 90°K) were also taken at $\phi=17°$ and 72° for Ho_2O_3 and at 20° and 72° for Er_2O_3, with similar results. The widths of the lines did not change measurably with angle indicating that exchange interaction is probably small.

In these patterns the lines appear to broaden

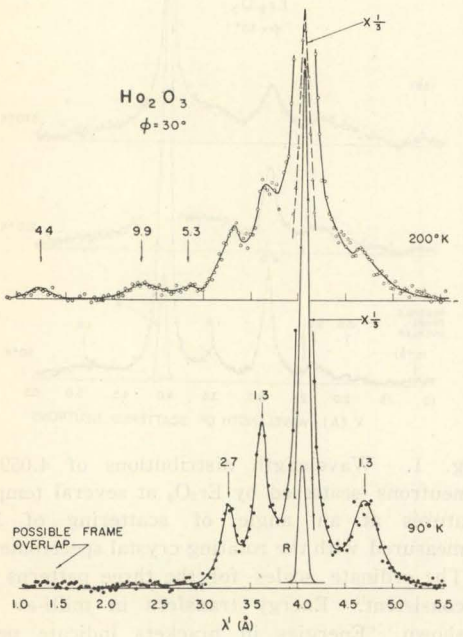

Fig. 2. Wavelength distributions for Ho_2O_3.

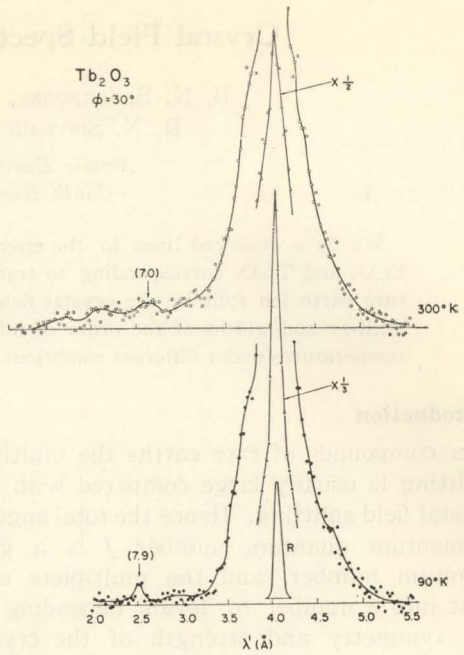

Fig. 3. Wavelength distributions for Tb_2O_3.

as the temperature is raised. This may be partly due to the appearance of additional unresolved lines, but it is believed that there is also a real broadening arising from the finite lifetimes (perhaps produced by modulation of the crystal field by lattice vibrations). At 90°K the line widths are ~0.7 milli-ev. This is much larger than estimated widths due to dipole-dipole interaction, but is reasonable for spin-lattice interaction[4].

Beryllium filter method

We have also made measurements using the beryllium detector method[5]. The pattern for Ho_2O_3 at 90°K is shown in Fig. 4. The peak at 47 milli-ev corresponds to that observed with the time of flight spectrometer in energy gain at about 44 milli-ev. Another, probably real, peak at 56 milli-ev is not resolved. Weak spurious peaks corresponding to energies of 12, 15, 25 and 37 milli-ev appeared in patterns for Er_2O_3, Tb_2O_3 and Ho_2O_3 as well as in non-magnetic Lu_2O_3. These spurious peaks were found to arise from Debye-Scherrer lines, which were sufficiently intense to penetrate the beryllium filter. In Er_2O_3 weak peaks, thought to be real, were observed at about 54 and 65 milli-ev. The energies of the peaks in Ho_2O_3 and Er_2O_3 are

higher (by a factor of about 2) than the typical crystal field splittings found in other rare earth compounds. However the oxides are particularly strongly bound and it is not surprising that the crystal field is correspondingly stronger.

Multiple chopper results

Measurements on Ho_2O_3 at 296°K were also made using a double chopper time of flight spectrometer[6]. With this instrument a large range of momentum transfer (Q) could be studied. Energy distributions observed at scattering angles of 12.5° and 155.4° for neutrons of initial energy 0.096 ev are shown in Fig. 5. Peaks corresponding to energy transfers of about 47 milli-ev can be seen for both energy loss and gain. The intensities are much reduced at 155.4°. Fig. 6 shows the variation of intensity with Q where the points are compared with the known magnetic form factors[7]. The agreement indicates that this peak is magnetic in origin. The intensities of the other peaks (Figs. 1—3) as a function of scattering angle, though measured over a much smaller range of Q, show the same general behaviour.

The results reported here are in substantial agreement with less extensive measurements reported by Cribier and Jacrot[8] since this work was commenced.

The authors would like to thank Dr. B. G. Haywood for his cooperation during the experiments performed with the double chopper.

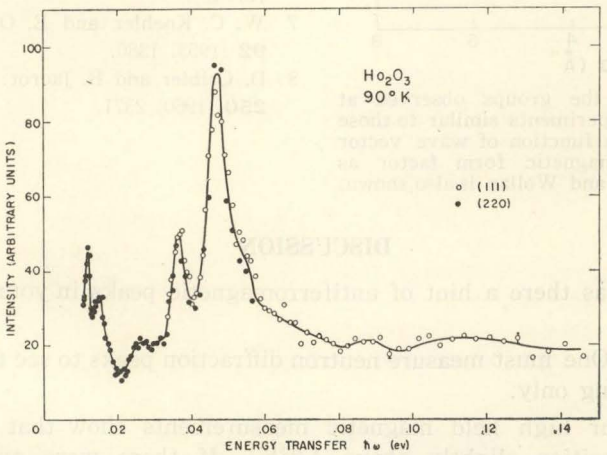

Fig. 4. Energy distributions of neutrons scattered through an angle of 45° by Ho_2O_3 at 90°K, measured using the beryllium detector method (fixed $E'=3$ milli-ev). The two different symbols correspond to the aluminum monochromator planes employed. The peaks at 12, 15, 25 and 37 milli-ev are spurious (see text).

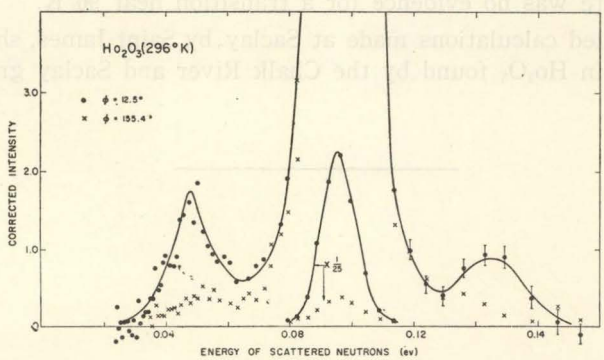

Fig. 5. Energy distributions of neutrons scattered at two angles by Ho_2O_3 at room temperature, measured using the multiple chopper/time-of-flight spectrometer with an incoming energy of 0.096 ev.

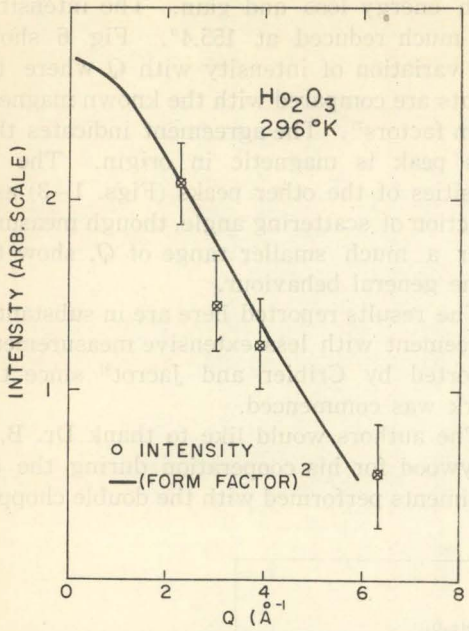

Fig. 6. Intensity of the groups observed at different angles in experiments similar to those in Fig. 5, plotted as a function of wave vector transfer Q. The magnetic form factor as measured by Koehler and Wollan is also shown.

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DISCUSSION

W.E. HENRY: Was there a hint of antiferromagnetic peaks in your neutron data on Er_2O_3 at 90°K?

A.D.B. WOODS: One must measure neutron diffraction peaks to see this. We observe incoherent scattering only.

W.E. HENRY: Our high field magnetic measurements show that there is an antiferromagnetic transition slightly above 4.2°K. If there were another at higher temperature, one could speculate on the applicability of the Yaffet-Kittel generalized treatment to this substance.

M.K. WILKINSON: Unpublished neutron diffraction results which were made several years ago by our group at Oak Ridge showed the antiferromagnetic transition at about 5°K, but there was no evidence for a transition near 90°K.

B. JACROT: Detailed calculations made at Saclay by Saint-James, show no indication for the 47 mv line in Ho_2O_3 found by the Chalk River and Saclay groups.