OPTICAL SPECTRA OF FERROELECTRIC-ANTIFERROMAGNETIC RARE EARTH MANGANATES

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The first optical measurement of the simultaneously ferroelectric and antiferromagnetic materials YbMnO₃, TmMnO₃, and YbMnO₃ are reported. Generally the spectra are characterized by a wide transmission window in the near infrared. For YbMnO₃ and TmMnO₃ sharp rare earth crystal field absorption lines are found within the window. As a consequence of anisotropic Mn³⁺⁻Yb³⁺ exchange interaction some of the Yb³⁺ lines are exchange split. A crystal field model of the Yb³⁺ spectra is presented.

The hexagonal heavy rare earth manganates [1,2] (R MnO₃; R = Ho, Er, Tm, Yb, Lu and Y, Sc) exhibit a rather unique set of physical properties, and may have some potentiality for practical applications [3]. They order in triangular antiferromagnetic states [4,5] with Néel temperatures in the liquid nitrogen range. The magnetism arises mainly from the trivalent manganese [6,7], which has the 3d⁴ electronic configuration. Furthermore, these compounds are ferroelectric with high Curie temperatures [8] (≈ 500°C) and very fast switching speeds [9] (≈ 10⁻⁷ sec).

We report here the first optical measurements on single crystals of YbMnO₃, TmMnO₃, and YbMnO₃. YbMnO₃ is opaque from the UV (50 000 cm⁻¹) down to the near infrared. At room temperature, the absorption, which apparently is associated with Mn³⁺, drops off at an "absorption edge" located at 10 300 cm⁻¹. As the temperature falls, this Urbach-like absorption edge moves higher energy, being 12 500 cm⁻¹ at 4ºK. Below the absorption edge, the crystal is quite transparent down to the deep infrared, where the phonon spectrum starts to rise near 1000 cm⁻¹. This wide "window" in the near infrared and the ferroelectricity of these materials should make them valuable as non-linear optical media [11].

In TmMnO₃ and YbMnO₃, there is superimposed on this background Mn³⁺ spectrum a host of sharp absorption lines in the window region which are due to transitions among rare earth crystal field energy levels. In this report we concentrate our attention on the YbMnO₃ spectrum. The intensities of many of the Yb³⁺ lines show marked dependence on temperature and below the Néel temperature some of the lines split into two or more components suggestive of exchange splittings [12]. As we sketch below, we have been able to interpret the Yb³⁺ spectrum in terms of calculated crystal fields, anisotropic Mn³⁺⁻Yb³⁺ exchange interactions, and phonon effects.

The compounds have the space group symmetry C₃ᵥ (P6₃ cm) [1]. In the hexagonal unit cell containing six formula units, two Yb³⁺ ions occupy sites with C₃ᵥ local symmetry and the other four occupy the slightly more distorted sites with C₃ symmetry. The rare earth ions at both sites are 8-fold coordinated, being situated between a pair of inverted tripyramids oriented along the c-axis.

In the point charge approximation [13], we have calculated the crystal field energy levels of Yb³⁺ at both sites. The crystal field lattice sums Aₖ were performed on a digital computer including approximately 5000 ions. There is excellent convergence for all terms except A₁² which has a mild convergence. We used the following values of mean radii:

\[ \langle r^2 \rangle = -0.022 \text{ Å}^2 \quad \langle r^4 \rangle = 0.165 \text{ Å}^4 \quad \langle r^6 \rangle = 1.064 \text{ Å}^6 \]

which are consistent, in both magnitude and sign, with the parameters for YbGG [14] and Yb:YGG [15]. These values differ significantly from...
Freeman-Watson's \( \langle J^2 \rangle \) [16], which did not give as good a fit to observations. We obtained the crystal field energy levels, given in fig. 1, by diagonalizing the Hamiltonian

\[
H_C = \sum_{n,m} \rho_n \langle J^2 \rangle A_n^m O_m^\dagger
\]

in the \( |J S J J_z \rangle \) representation. Using the calculated crystal field parameters to make the assignment of line A at both sites as shown in fig. 1, all lines listed as "crystal field" in table 1 follow immediately. The poorest fit is a deviation of 1% between calculation and the center of gravity of lines Q, R, S, and T. In view of the simple nature of the point charge model, the agreement is remarkably good. As an additional measure of the reliability of the fit, the derived spin-orbit constants \( \lambda = -2889 \text{ cm}^{-1} \) for \( C_{3v} \) sites and \( \lambda = -2876 \text{ cm}^{-1} \) for \( C_3 \) sites compare favorably with \( \lambda = -2880 \text{ cm}^{-1} \) for \( \text{Yb}^{3+} \) in \( \text{YbGG} \) [14].

From the example of the garnets [14], we expect some of the absorption lines to be phonon-related to the first strong line of electronic transition. We obtained the phonon "difference" sidebands as local maxima on the long wavelength shoulder of the first transition line A. A reflection about line A gives lines D, G, N and U as phonon "summation" sidebands of A. They involve two types of phonons, as shown in table 1.

We now turn to the most interesting feature of the \( \text{Yb}^{3+} \) spectrum, namely the exchange splitting of the crystal field spectrum. As an example of this effect, we find that the high tem-
Table 1

<table>
<thead>
<tr>
<th>Label</th>
<th>Observations (cm⁻¹)</th>
<th>Calculations (cm⁻¹)</th>
<th>Comment</th>
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<tr>
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<td>10449</td>
<td>10444</td>
<td>2 phonons-1 a)</td>
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<td>F</td>
<td>10506</td>
<td>10507</td>
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<td>I</td>
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<td></td>
<td></td>
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<tr>
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<td>1 phonon-II b)</td>
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<tr>
<td>U</td>
<td>11297</td>
<td>11302</td>
<td>2 phonons-II b)</td>
</tr>
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</table>

a) Phonon-I = 77 cm⁻¹; b) Phonon-II = 506 cm⁻¹.

The observed crystal field spectrum of Yb³⁺ in YbMnO₃, observed at 4.8 K, is shown in the figure. The observed and calculated transition frequencies are listed in the table. The splitting of the 10571 cm⁻¹ line into two components is consistent with the crystal field splitting expected for the Yb³⁺ ion in this compound. The temperature dependence of the splitting is described by the equation

\[ \Delta(T)/\Delta(0) = B(1 - T/T_N)^\beta \]

to our data in the region 0.900 < T/T_N < 0.999 gives β = 0.329, B = 1.464. Thus, we conclude that the splitting arises from an interaction between Yb³⁺ and the Mn³⁺ sublattice magnetization.

The microscopic origin of this exchange splitting may be understood by referring to fig. 4 where we note that the two rare earth sites have significantly different magnetic environments. We assume at the outset that the rare earth spin S₀ is coupled to the Mn³⁺ spins S_Mn by an anisotropic exchange interaction of the form

\[ H_E = \sum_{i=1}^{6} S_0 \cdot A_{ij} \cdot S_{Mn}^i \]

where A is the exchange tensor. In a suitably
rotated coordinate system this Hamiltonian can be reduced to

\[ H_E = 3S_2^0 (A_{XX} - A_{XY}) S \quad \text{for } C_{3v} \text{ sites}, \]

\[ H_E = 3S_2^0 \left[ -\frac{1}{2}(A_{XX} - A_{Z2X}) + \frac{1}{2}\sqrt{3}(A_{ZXY} + A_{XY}) \right] S \]

for \( C_3 \) sites, where \( S \) is the magnitude of the \( Mn^{3+} \) spin. \( A_{XX}, A_{XY} \) couple to \( Mn^{3+} \) spins above the rare earth ion and \( A_{XY}, A_{ZXY} \) to those below it. We note here that, contrary to the case of the garnets [12], the isotropic part of the exchange interactions will not give a splitting in our case at all. Furthermore, noting from fig. 3 that the longer superexchange paths subtend more favorable angles, we expect \( A_{XX} \) and \( A_{ZXY} \) to be nearly equal and arrive at the remarkable conclusion that there should be a negligible splitting at \( C_{3v} \) sites and a finite splitting at \( C_3 \) sites. This expectation is confirmed by our observation.

REFERENCES