

OPTICAL SPECTRA OF FERROELECTRIC - ANTIFERROMAGNETIC  
RARE EARTH MANGANATES \*

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The first optical measurement of the simultaneously ferroelectric and antiferromagnetic materials  $\text{YMnO}_3$ ,  $\text{TmMnO}_3$  and  $\text{YbMnO}_3$  are reported. Generally the spectra are characterized by a wide transmission window in the near infrared. For  $\text{YbMnO}_3$  and  $\text{TmMnO}_3$  sharp rare earth crystal field absorption lines are found within the window. As a consequence of anisotropic  $\text{Mn}^{3+}$ - $\text{Yb}^{3+}$  exchange interaction some of the  $\text{Yb}^{3+}$  lines are exchange split. A crystal field model of the  $\text{Yb}^{3+}$  spectra is presented.

The hexagonal heavy rare earth manganates [1,2] ( $\text{RMnO}_3$ ; 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  $3d^4$  electronic configuration. Furthermore, these compounds are ferroelectric with high Curie temperatures [8] ( $\approx 700^\circ\text{C}$ ) and very fast switching speeds [9] ( $\approx 10^{-7}$  sec).

We report here the first optical measurements on single crystals of  $\text{YMnO}_3$ ,  $\text{TmMnO}_3$ , and  $\text{YbMnO}_3$ .  $\text{YMnO}_3$  is opaque from the UV ( $50\,000\text{ cm}^{-1}$ ) down to the near infrared. At room temperature, the absorption, which apparently is associated with  $\text{Mn}^{3+}$ , drops off at an "absorption edge" located at  $10\,300\text{ cm}^{-1}$ . As the temperature falls, this Urbach-like [10] absorption edge moves to higher energy, being at  $12\,500\text{ cm}^{-1}$  at  $4^\circ\text{K}$ . Below the absorption edge, the crystal is quite transparent down to the deep infrared, where the phonon spectrum starts to rise near  $1000\text{ cm}^{-1}$ . This wide "window" in the near infrared and the ferroelectricity of these materials should make them valuable as non-linear optical media [11].

In  $\text{TmMnO}_3$  and  $\text{YbMnO}_3$ , there is superimposed on this background  $\text{Mn}^{3+}$  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  $\text{YbMnO}_3$  spectrum. The intensities of many of the  $\text{Yb}^{3+}$  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  $\text{Yb}^{3+}$  spectrum in terms of calculated crystal fields, anisotropic  $\text{Mn}^{3+}$ - $\text{Yb}^{3+}$  exchange interactions, and phonon effects.

The compounds have the space group symmetry  $C_{6v}^3$  ( $P6_3\text{ cm}$ ) [1]. In the hexagonal unit cell containing six formula units, two  $\text{Yb}^{3+}$  ions occupy sites with  $C_{3v}$  local symmetry and the other four occupy the slightly more distorted sites with  $C_3$  symmetry. The rare earth ions at both sites are 8-fold coordinated, being situated between a pair of inverted tripiramids oriented along the  $c$ -axis.

In the point charge approximation [13], we have calculated the crystal field energy levels of  $\text{Yb}^{3+}$  at both sites. The crystal field lattice sums  $A_n^m$  were performed on a digital computer including approximately 5000 ions. There is excellent convergence for all terms except  $A_2^0$  which has a mild convergence. We used the following values of mean radii:

$$\langle r^2 \rangle = -0.022 (\text{\AA})^2 ; \quad \langle r^4 \rangle = 0.165 (\text{\AA})^4 ;$$

$$\langle r^6 \rangle = 1.064 (\text{\AA})^6$$

which are consistent, in both magnitude and sign, with the parameters for  $\text{YbGG}$  [14] and  $\text{Yb:YGG}$  [15]. These values differ significantly from

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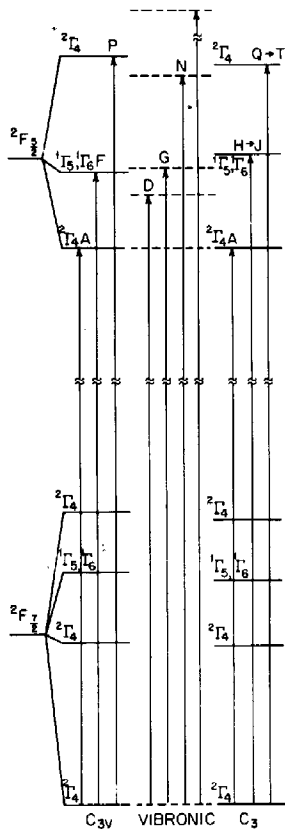


Fig. 1. Crystal field and vibronic energy levels of  $\text{Yb}^{3+}$  in  $\text{YbMnO}_3$ .

Freeman-Watson's  $\langle r^n \rangle$  [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

$$H_C = \sum_{n,m} \theta_n \langle r^n \rangle A_n^m O_n^m$$

in the  $|LSJ_z\rangle$  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  $\lambda = -2869 \text{ cm}^{-1}$  for  $\text{C}_{3v}$  sites and  $\lambda = -2876 \text{ cm}^{-1}$  for  $\text{C}_3$  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-

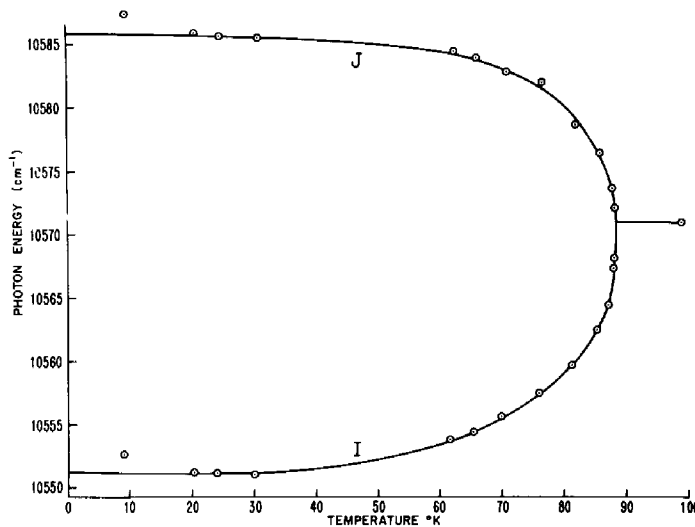


Fig. 2. Positions of lines I and J in spectrum of  $\text{YbMnO}_3$ .

Table 1  
Observed and calculated crystal field and vibronic spectrum of Yb<sup>3+</sup> in YbMnO<sub>3</sub>. Observation at 4.8°K.

Label	Observations (cm <sup>-1</sup> )	Calculations (cm <sup>-1</sup> )			Comment
		C <sub>3</sub>	C <sub>3v</sub>	vibronic	
A	10290	10290	10290	-----	fit
D	10449	-----	-----	10444	2 phonons-I <sup>a)</sup>
F	10506	-----	10507	-----	crystal field
G	10524	-----	-----	10521	3 phonons-I <sup>a)</sup>
H	10541	}	10570	-----	crystal field exchange split
I	-----				
F'	10560				
J	10584	}	-----	-----	1 phonon-II <sup>b)</sup>
N	10791				
P	10855	-----	10854	-----	crystal field
Q	10905	}	10829	-----	crystal field exchange split
R	10935				
S	10953				
T	10983				
U	11297	-----	-----	11302	2 phonons-II <sup>b)</sup>

a) Phonon-I = 77 cm<sup>-1</sup>; b) Phonon-II = 506 cm<sup>-1</sup>.

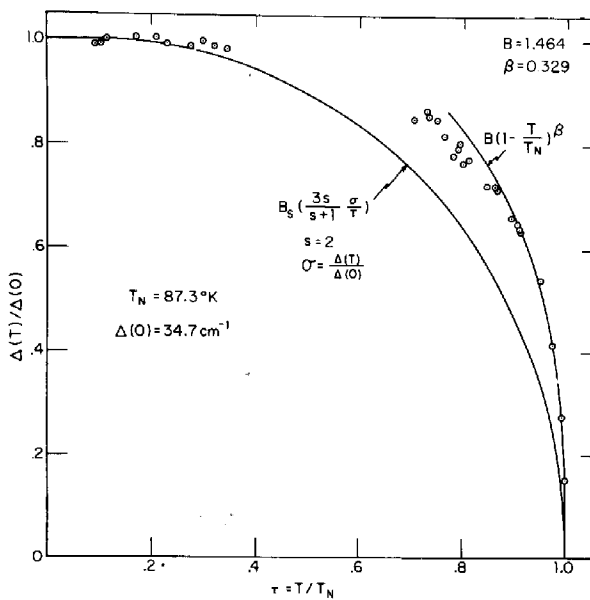


Fig. 3. Exchange splitting of Yb<sup>3+</sup> crystal field transition at 10571 cm<sup>-1</sup> and critical phenomena parameters of YbMnO<sub>3</sub>.

perature line at 10571 cm<sup>-1</sup> splits almost symmetrically into two lines below 85°K (fig. 2). Fig. 3 shows that the separation of the split lines follows a characteristic magnetization curve yielding T<sub>N</sub> = 87.3°K for YbMnO<sub>3</sub> which agrees well with an interpolation from neutron diffraction determinations of T<sub>N</sub> of other rare earth manganates [6]. Using a zero temperature splitting of Δ(0) = 34.7 cm<sup>-1</sup>, a least squares fit of the critical phenomena [17] expression

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

to our data in the region 0.900 < T/T<sub>N</sub> < 0.999 gives β = 0.329, B = 1.464. Thus, we conclude that the splitting arises from an interaction between Yb<sup>3+</sup> and the Mn<sup>3+</sup> 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 S<sup>0</sup> is coupled to the Mn<sup>3+</sup> spins S<sup>i</sup><sub>Mn</sub> by an anisotropic exchange interaction of the form

$$H_E = \sum_{i=1}^6 S^0 \cdot A^{(i)} \cdot S^i_{Mn}$$

where A is the exchange tensor. In a suitably

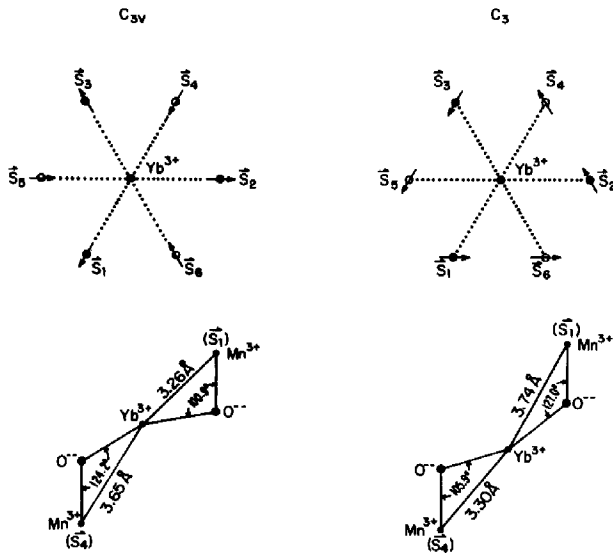


Fig. 4. Exchange fields at the two rare earth sites.  $S_1, S_2, S_3$  above  $Yb^{3+}$ ,  $S_4, S_5, S_6$  below  $Yb^{3+}$ .

rotated coordinate system this Hamiltonian can be reduced to

$$H_E = 3S_z^0 (A_{zx} - A'_{zx})S \quad \text{for } C_{3v} \text{ sites,}$$

$$H_E = 3S_z^0 \left[ -\frac{1}{2} (A_{zx} - A'_{zx}) + \frac{1}{2}\sqrt{3} (A_{zy} + A'_{zy}) \right] S$$

for  $C_3$  sites, where  $S$  is the magnitude of the  $Mn^{3+}$  spin.  $A_{zx}, A_{zy}$  couple to  $Mn^{3+}$  spins above the rare earth ion and  $A'_{zx}, A'_{zy}$  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  $A_{zx}$  and  $A'_{zx}$  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.

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