POLARIZED ELECTRONIC RAMAN EFFECT OF TRIVALENT EUROPIUM IN YTTRIUM VANADATE*

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To our knowledge no photoelectrically recorded polarized electronic Raman effects have yet been reported. In this note we want to report on the observation and interpretation of such an effect for the trivalent europium ion embodied in the tetragonal host lattice yttrium vanadate.

Raman spectra of crystals doped with trivalent lanthanide ions excited with conventional mercury sources or lasers operating in the green region of the spectrum are in general obscured by the presence of fluorescence lines. These complications almost never arise if the 6328-Å radiation of the He-Ne laser is used as the excitation source.

One of us has recently reported on an electronic Raman study of trivalent europium in the host lattice yttrium gallium garnet.[1] Because of the complexity of assigning the lattice modes and the fact that the orientation of the crystallographic axis was unknown, polarization studies of single crystals were not performed. For the crystals investigated here the orientations of the crystallographic axis were initially not known. We have recently shown,[2] however, that provided a reasonable a priori knowledge of the vibrational levels of the host crystal is available, it is possible to determine the orientation of the crystal from the polarization properties of the vibrational Raman lines.

The europium ions replace the yttrium ions of YVO_4 and thus occupy sites of D_{2d} symmetry.[3] The crystal field components of the split LSJ manifolds of the Eu^{3+} ions may be labeled according to the irreducible representations of the point group D_{2d}. The site symmetry of the vanadium ion is also D_{2d} and thus vibrational levels of the VO_4^{3-} group are also classified according to these representations. The selection rules for vibrational as compared to electronic transitions may, however, be different even if both are classified under the same point group. Whereas the scattering tensor for the vibrational case is symmetric, this is not necessarily true for the electronic effect.[4] The difference in the case of the point group D_{2d} is indicated in Table I. The electronic levels of $^7F_{0,1,2}$ in the crystal field of europium in yttrium vanadate are labeled with A_1, B_2+E, and $A_1+B_1+B_2+E$, respectively. It is seen that the crucial representation A_2 does not occur. Thus, the selection rules for the vibrational as well as the electronic Raman transitions are identical since the electronic ground state of Eu^{3+} has symmetry A_1.

Table I. Activity representations for the point-group D_{2d} scattering tensor.

Rep.	Vib.	Electronic
A_1	$xx+yy, zz$	$xx+yy, zz$
A_2		$xy-yz$
B_1	$xx-yy$	$xx-yy$
B_2	$xy+yx$	$xy+yx$
E	yz, zx	yz, zx

Figure 1 shows the Raman spectrum of YVO_4:Eu^{3+} in the range 100-600 cm^{-1}. The experimental technique and the assignment of the stronger lines in the spectrum has been described elsewhere.[2] The Raman line at 404.5 cm^{-1} has not been observed in the spectrum of a single crystal of YVO_4 doped with Nd^{3+} and must thus be of electronic origin. In Fig. 2, the polarization properties of this line are compared with the same properties of two vibrational lines of symmetry B_1 and E. It is obvious that the line at 404.5 cm^{-1} belongs to representation E.

The temperature dependence of the Raman

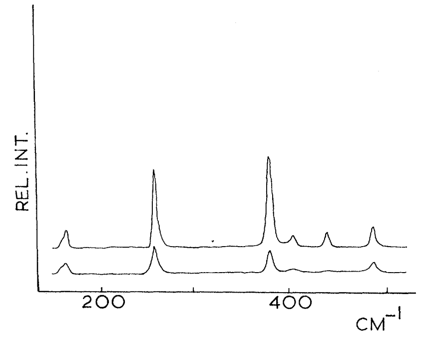

FIG. 1. The Raman spectrum of YVO_4:Eu at 100°K. The upper curve is for laser polarization Oy; the lower, for Ox. Slit width 4 cm^{-1}, $T=3$ sec.

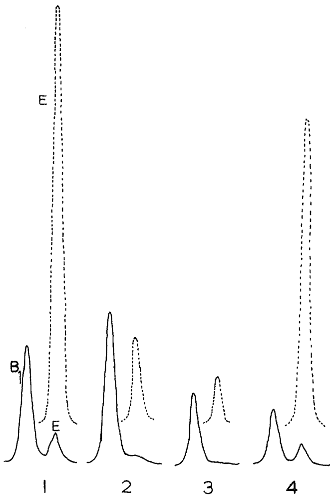

FIG. 2. Polarization properties of the Raman line at 404.5 cm^{-1} (E, lower trace) compared to a vibrational E mode at 840 cm^{-1} (E, upper trace). The numbers refer to four different combinations of polarization of incident and scattered radiation.

spectrum has also been determined. In contrast to all vibrational lines, the half-width of the line at 404.5 cm^{-1} decreases strongly upon cooling the sample.

The two levels of the crystal-field split ${}^7F_1$ manifold of Eu^{3+} are expected to be located some 300-450 cm^{-1} above the ground state ${}^7F_0$. A reported[5] crystal field analysis of Eu in YVO_4 indicates that the parameter $A_2{}^0$ is negative, thus placing the E level at higher energy than the B_2 level. We can thus correlate the observed Raman line with a shift of 404.5 cm^{-1} with the electronic level of the ${}^7F_1$ manifold of symmetry E.

The fluorescence spectrum of this particular single crystal has also been investigated. Four strong lines have been reported between 5930 and 6200 Å. They represent the well known ${}^5D_0$-${}^7F_{1,2}$ transitions. The frequencies of these transitions together with their assignments are given in Table II.

Table II. Fluorescence and Raman data for Eu:YVO_4

Fluorescence	Assignment	Energy levels	Raman lines
16840		362	360
16798	${}^7F_1$	404.5	404.5
16238		964	970
	${}^7F_2$		995
			1018
16133		1069	1067
	${}^5D_0$	17202.5	

The position of the E level found from the Raman experiments then immediately gives the position of the ${}^5D_0$ level as well as the levels of the split ${}^7F_1$ and ${}^7F_2$ manifolds. These positions are also indicated in Table II, and it is seen that in the region of interest of Raman experiments a total of four electronic lines are expected.

Further, very weak Raman lines of presumably electronic origin have been found at 359.5 cm^{-1} and between 950 and 1075 cm^{-1}. Because of the weakness of these Raman lines their exact polarization properties were not determined, but the incomplete polarization data for the line at 359.5 cm^{-1} are in good agreement with an assumed B_2 assignment.

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[1] J. A. Koningstein, to be published.

[2] J. A. Koningstein and O. Sonnich Mortensen, to be published.

[3] Strukturbericht, edited by P. Niggli, P. P. Ewald, K. Fajans, and M. v. Laue (Akademische Verlagsgesellschaft m.b.H., Leipzig, Germany, 1937), Vol. 3.

[4] G. Placzek, in Handbuch der Radiologie (Leipziger Vorträge, Leipzig, Germany, 1934) Vol. 6, Part 2, p. 205.

[5] C. Brecher, H. Samelson, and A. Lempicki, "Abstracts of Conference on Optical Properties of Ions in Crystals," The Johns Hopkins University, September, 1966 (unpublished).