Dependence of the $E_1$ Reflectivity Structure in EuO on Temperature and Doping

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The temperature dependence of the $E_1$ reflectivity peak ($4f^7\rightarrow 4f^55d$ transition) in both intrinsic and Gd-doped single crystal EuO over the range 200–300 K has been measured. It is observed that this structure occurs consistently at lower energies in Gd-doped EuO vis-a-vis intrinsic for all temperatures covered. X-ray data indicate a smaller lattice constant for the doped material thus substantiating the direction of the shift on the basis of an overlap model. A strong Burstein–Moss effect would have shifted the peak oppositely to that observed. The onset of the "red shift" associated with magnetic ordering in the bulk occurs at a higher temperature for the doped material consistent with its higher $T_c$, but the shift is not as closely correlated with this temperature as it is for intrinsic EuO. These results suggest a localized model for the $E_1$ excitation.

In this note we present some measurements of the influence of doping and temperature on the $E_1$ reflectivity structure in EuO.¹ The origin of this structure, ignoring band effects, arises from the $4f^7(^8S_{7/2})\rightarrow 4f^6(^{1}F_{7/2})5d(T_{2g})$ multiplet optical transitions of the Eu$^{2+}$ ion in a cubic crystal field.²

Single crystal samples of both intrinsic and Gd-doped EuO were supplied by M. Shafer of the IBM Research Laboratory in Yorktown Heights. The properties of the two crystals investigated are given in Table I. The amount of Gd in the doped sample was determined with an electron-beam microprobe and the lattice constants by powder x-ray diffraction. The Curie temperature of the doped material was found to be 120–125 K using a force magnetometer. Resistivities were not measured accurately but the Gd content, preparation, and Curie temperature of the doped specimen follow very closely samples whose transport properties were reported on by von Molnar and Shafer.³ Therefore we will assume their values of resistivity ($10^{-2}$ Ω cm) and carrier concentration ($n\approx 3\times 10^{20}$ cm$^{-3}$) as nominal for our sample.

It is interesting to speculate what sort of Burstein–Moss shift might be expected with such high carrier concentrations. Taking the $t_{2g}$ bandwidth to be 0.6 eV⁴ gives an estimate of $m^*/m\approx 3$ in a simple tight binding approximation. Using Moss's equation⁵ for the energy shift of an optical transition whose final state is a simple parabolic conduction band results in an anticipated upward shift of 0.07 eV. However, we see from Figs. 1 and 2 and Table I that the $E_1$ reflectivity peak and minimum actually undergo a shift downwards in energy of 0.058 and 0.032 eV, respectively, under the influence of Gd doping.

On the other hand, let us consider what the effect of the observed lattice contraction would be on this structure. The dependence of the $E_1$ absorption peak on lattice constant in sputtered films of EuO has been measured by Lee and Suita.⁶ With their results and the change in $a_0$ noted in Table I, we would expect a downward shift of 0.047 eV which is in reasonable agreement with our observations. Thus we conclude that there is essentially no evidence of a Burstein–Moss effect and the observed shift in the $E_1$ structure can be accounted for by the lattice constant change. Even allowing that the $E_1$ structure is probably built up from a superposition of many exciton like multiplet excitations, one feels that such a large number of free carriers lying close by in energy should in some way influence its behavior.

Fig. 1. Temperature dependence of the $E_1$ reflectivity peak in intrinsic and Gd-doped EuO.

An explanation may be found in Kasuya's model⁷ which places the $X_2$ conduction band minimum about 1.2 eV above the $\Gamma_1$ minimum. Thus the free carriers would tend to pool in $\Gamma_1$ or an impurity band below it where they would not interact with the states involved in the $E_1$ transitions.

We next turn to the temperature dependence of the $E_1$ structure in the paramagnetic region. The results

1771
are summarized in Table I. We see that the temperature coefficients are opposite in sign and larger in magnitude than those reported for the absorption edge. Temperature and pressure coefficients of optical transitions are related by the following relation:

\[(\partial E/\partial T)_P = (\partial E/\partial T)_T + (\alpha/\beta)(\partial E/\partial P)_T,\]

where \(\alpha\) is the volume thermal expansion constant and \(\beta\) the compressibility. The term on the left is the measured temperature coefficient while the second term on the right represents the dilatation contribution. The constant volume term, \((\partial E/\partial T)_T\), contains the electron-phonon or thermal broadening contribution. For many semiconductors this term is considerably greater than the dilatation factor. We will investigate the situation for EuO by inferring a pressure coefficient for the \(E_1\) structure from the previously mentioned thin film data in conjunction with compressibility figures. This analysis leads to a value of about 10 meV/kbar for \((\partial E/\partial P)_T\) or 4.2\(\times\)10^{-4} eV/K for the dilatational component of the measured temperature coefficient 5.1\(\times\)10^{-4} eV/K. The closeness of these two results indicates that EuO behaves differently in this regard than many of the more usual semiconductors.

Finally we note that the data of Figs. 1 and 2 show the onset of the red shift in Gd-doped EuO not to be as closely correlated with \(T_e\) as is the case for intrinsic EuO. If the mechanism for exchange enhancement were of the RKKY-type one would expect the shift to be nearer the higher \(T_e\). That is not the case. We note that the mechanism producing the enhanced \(T_e\) and the mechanism which splits the \(E_1\) transition are not the same. A possibility might be that the enhanced \(T_e\) arises from exchange between the magnetic quasimolecules proposed by Kasuya and Nagaev with little coupling to individual Eu^{2+} spins outside the clusters. The red shift would then not manifest itself until somewhere near the intrinsic \(T_e\) with the onset of the usual indirect exchange interaction. It would appear that the relationship between macroscopic magnetization and the optical properties of doped Eu chalcogenides deserves more study than it has been previously given.

We are indebted to M. W. Shafer for supplying our crystals and to G. L. Ayers for technical assistance in performing the experiments.

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**Table I. Summary of Results.**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Doping</th>
<th>(a_0)</th>
<th>(T_e)</th>
<th>(E_{E1}^{RT})</th>
<th>((\partial E/\partial T)^{RT})</th>
</tr>
</thead>
<tbody>
<tr>
<td>EuO</td>
<td></td>
<td>5.143</td>
<td>69</td>
<td>1.548 (peak)</td>
<td>5.1\pm0.4 (peak)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.449 (min)</td>
<td>9.2\pm1.0 (min)</td>
</tr>
<tr>
<td>Gd:EuO</td>
<td>2.5</td>
<td>5.135</td>
<td>120</td>
<td>1.490 (peak)</td>
<td>2.9\pm0.4 (peak)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.417 (min)</td>
<td>9.2\pm1.0 (min)</td>
</tr>
</tbody>
</table>

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**Fig. 2.** Temperature dependence of the \(E_1\) reflectivity minimum in intrinsic and Gd-doped EuO. Note the reversal in sign of the temperature coefficient in the vicinity of \(T_e\) due to broadening caused by spin splitting of the final state.