

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 ($4f^7 \rightarrow 4f^6 5d$ transition) in both intrinsic and Gd-doped single crystal EuO over the range $20^\circ\text{--}300^\circ\text{K}$ 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 $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d(T_{2g})$ 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 $120^\circ\text{--}125^\circ\text{K}$ 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 ($10^{-3} \Omega \text{ cm}$) and carrier concentration ($n \approx 3 \times 10^{20} \text{ cm}^{-3}$) 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 eV ⁴ gives an estimate of $m^*/m \approx 3$ in a simple tight binding approximation. Using Moss' 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 *downward* in energy of amount 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 Suits.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.

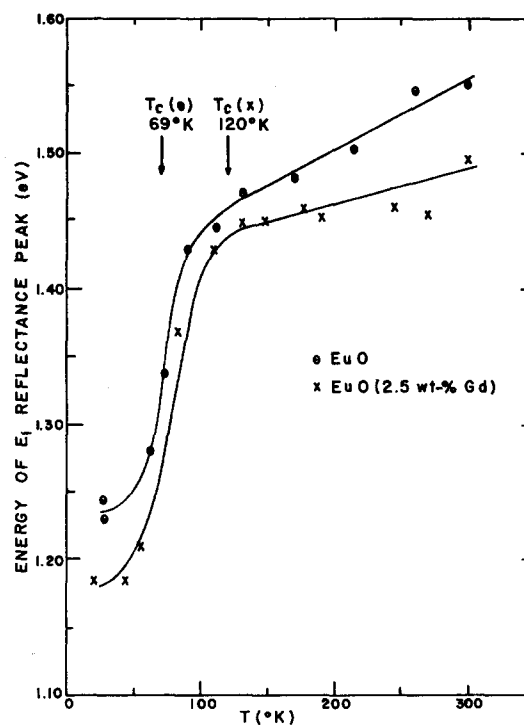


FIG. 1. Temperature dependence of the E_1 reflectivity peak in intrinsic and Gd-doped EuO.

An explanation may be found in Kasuya's model⁷ which places the X_3 conduction band minimum about 1.2 eV above the Γ_1 minimum. Thus the free carriers would tend to pool in Γ_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

TABLE I. Summary of results.

Crystal	Doping (wt% Gd)	a_0 (Å)	T_c (°K)	ρ_{RT} (Ω cm)	E_1^{RT} (eV)	$(\partial E_1/\partial T)_P^{RT}$ ($\times 10^{-4}$ eV/°K)
EuO	...	5.143	69	$\sim 10^8$	1.548 (peak) 2.449 (min)	5.1 \pm 0.4 (peak) 9.2 \pm 1.0 (min)
Gd:EuO	2.5	5.135	120	$\sim 10^{-3}$	1.490 (peak) 2.417 (min)	2.9 \pm 0.4 (peak) 9.2 \pm 1.0 (min)

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.⁸ Temperature and pressure coefficients of optical transitions are related by the following relation:

$$(\partial E/\partial T)_P = (\partial E/\partial T)_V + (\alpha/\beta)(\partial E/\partial P)_T, \quad (1)$$

where α is the volume thermal expansion constant and β 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, $(\partial E/\partial T)_V$, contains the electron-phonon or thermal broadening contribution. For many semiconductors this term is considerably greater than the dilatation factor.⁹ We will investigate the situation for EuO by inferring a pressure coefficient for the E_1 structure from the previously mentioned thin

film data⁶ in conjunction with compressibility figures.¹⁰ This analysis leads to a value of about 10 meV/kbar for $(\partial E/\partial P)_T$ or 4.2×10^{-4} eV/°K for the dilatational component of the measured temperature coefficient 5.1×10^{-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_c as is the case for intrinsic EuO. If the mechanism for exchange enhancement were of the RKKY-type¹¹ one would expect the shift to be nearer the higher T_c . That it is not suggests that the mechanism producing the enhanced T_c and the mechanism which splits the E_1 transition are not the same. A possibility might be that the enhanced T_c arises from exchange between the magnetic quasimolecules proposed by Kasuya¹² and Nagaev¹³ 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_c 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.

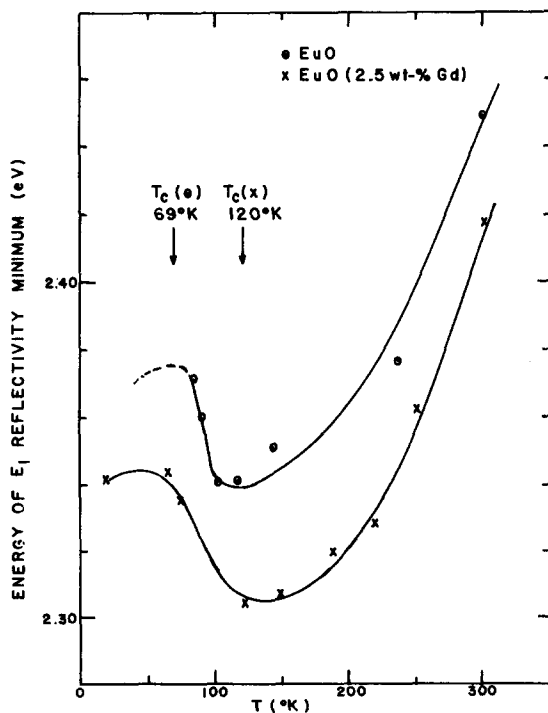


FIG. 2. Temperature dependence of the E_1 reflectivity minimum in intrinsic and Gd-doped EuO. Note the reversal in sign of the temperature coefficient in the vicinity of T_c due to broadening caused by spin splitting of the final state.

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