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PRESSURE DEPENDENCE OF THE ABSORPTION EDGE OF THE EUROPIUM-CHALCOGENIDES

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The room temperature pressure dependence of the absorption edge of EuO, EuS, EuSe and EuTe single crystals was found to be – 4.4; – 7.9; – 8.4 and – 12 meV/kbar respectively. Using these data the deformation potential was calculated.

THE EUROPIUM-chalcogenides have found the interest of many investigators because these substances are ferromagnetic semiconductors and offer the unique possibility to study various optical effects as well as transport phenomena in relation with the magnetic properties. A fundamental discovery in these materials has been the large red-shift of the absorption edge on cooling below the magnetic ordering temperature.[1–3] This and other exciting experiments have caught the interest of several theoreticians who proposed various models for the optical transitions and tried to explain the anomalous red-shift of the absorption edge. Some of these models assume for the optical transition near the absorption edge a $4f^7-4f^6 5d^1$ transition,[4,5] the red-shift being due to an exchange splitting of the excited state. In another model the red-shift is quantitatively explained by the splitting of a conduction band into spin-polarized sub-bands.[6,7] Recently, a further possibility was suggested by Callen[8] who invoked the magnetostriction as the cause of the red-shift. This proposal makes assumptions about the sign of the pressure dependence of the absorption edge and the deformation potentials and we thought it necessary to produce experimental evidence for this.

In a small chamber filled with silicon oil as the pressure transducing medium we measured the optical transmission of high quality (residual absorption for wavelengths larger than the absorption edge between 1 and 10 cm^{-1}) ground and polished single crystal plates of the Eu-chalcogenides. The crystals were brought under pressure in and out of the light path thus establishing a reference light beam system. The monochromatic light (from a high resolving Zeiss double monochromator) entered and left the pressure chamber by means of glass light pipes. Pressures up to 4 kbar have been used several times, though the usual pressure was not higher than 1 kbar to avoid damage of the system.

It was found that the transmission curves of all substances shifted parallel to itself to longer wavelengths upon application of pressure. Two methods of measurements have been used. The wavelength change under pressure was recorded for constant transmission intensity near the absorption edge or the change of transmission was measured for constant wavelength; with the slope of the transmission versus wavelength curve the shift in wavelength was computed. The latter method gave more precise results which are compiled in Fig. 1.

The compressibility $\mathcal{K}$ of EuO at room temperature has been measured by McWhan *et al.*[9] and Socolova *et al.*[10] to be about 1×10^{-6} bar^{-1} and by Stevenson *et al.*[11,12] to be 4.3 and 3.4×10^{-6} bar^{-1}. The discrepancy of a factor of 4 in these results is rather disturbing, however further discussions the latest published value 3.4 × 10^{-6} bar^{-1} [12] will be used. The change of lattice constant under pressure will then be

$$da/dp \;=\; -\mathcal{H}a_0/3 \;=\; -\,5.9\times 10^{-6}\ \text{Å/bar} \quad (1)$$

ing an a_0 for EuO of 5.14 Å. If one plots the sition of the absorption edge of the Eu-alcogenides against the lattice constant one tains a nearly straight line with a slope $_G/da = 0.65$ eV/Å. We can now compute the ift of the absorption edge with pressure

$$\begin{aligned} dE_G/dp &= dE_G/da\,.\,da/dp \\ &= -\,3.85\times 10^{-6}\ \text{eV/bar} \quad (2) \end{aligned}$$

hich should be compared with the experimental lue of $dE_G/dp = -\,4.4\times 10^{-6}$ eV/bar.

The small discrepancy arises of course, ecause we have assumed that the variation of e energy gap with the lattice constant by xchanging the anion is the same as by applying ressure to one single material, an assumption hich cannot be correct since it neglects co-alency effects of the anions. However, the alculation gives the correct sign and the right rder of magnitude of the shift.

The measurement of the pressure dependence f the absorption edge enables us to separate he dilatational part from the phonon part of the hift of the absorption edge with temperature. t can easily be shown that

$$\begin{aligned} (dE_G/dT)_{\mathrm{dil}} &= -3\beta/\mathcal{H}\, dE_G/dp \\ &= +\,0.51\times 10^{-4}\ \text{eV/K} \quad (3) \end{aligned}$$

here β is the *linear* coefficient of thermal xpansion which for EuO is $13.2\times 10^{-6}\ \mathrm{K}^{-1}$ [13,14] t room temperature. The total shift of the bsorption edge with temperature in the para-agnetic region is the sum of the dilatational nd phonon part and has been measured separ-tely, i.e.:

$$\begin{aligned} (dE_G/dt)_{\mathrm{tot}} &= (dE_G/dT)_{\mathrm{dil}} + (dE_G/dT)_{\mathrm{ph}} \\ &= -\,1.4\times 10^{-4}\ \text{eV/K} \quad (4) \end{aligned}$$

Thus $(dE_G/dT)_{\mathrm{ph}} = -\,1.9\times 10^{-4}$ eV/K.

According to Bardeen and Shockley[15] the shift of the energy gap with dilatation of the lattice Δ equals

$$\begin{aligned} dE_G/d\Delta &= 2/3(\epsilon_v-\epsilon_c) = -1/\mathcal{H}\,(dE_G/dp) \\ &= +\,1.29\ \text{eV} \quad (5) \end{aligned}$$

$$\text{or } (\epsilon_v-\epsilon_c) = +\,1.94\ \text{eV}$$

where ϵ_v and ϵ_c are the defomation potentials of the valence- and conductionbands respectively.

The *difference* in the defomation potentials will not be very temperature dependent, since $1/\mathcal{H}\,(dE_G/dp)$ is nearly temperature independent, which can be seen by rewriting (2):

$$\begin{aligned} (1/\mathcal{H})(dE_G/dp) &= (1/\mathcal{H})(dE_G/da\ da/dp) \\ &= -\,dE_G/da\,.\,a_0/3. \quad (6) \end{aligned}$$

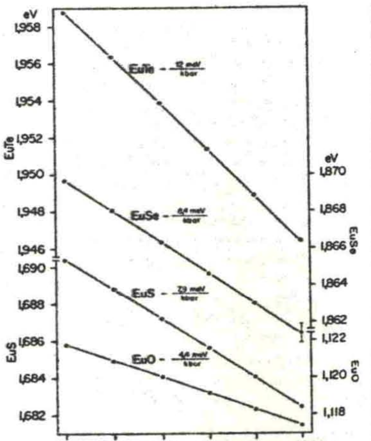

FIG. 1. Pressure dependence of the optical absorption near the absorption edge of the Eu-chalcogenides.

If we take dE_G/da at *low temperatures* from a plot of the position of the absorption edge of the Eu-chalcogenides against the lattice constant we realize that it changes only by about 10 per cent of the value at room temperature (a_0 changes by about 1‰).

We therefore can compute the shift of the absorption edge due to magnetostriction by using (5) and inserting the measured $d\Delta$ of $-\,3.10^{-3}$.[13,14] It is found that $dE_G = -\,3.88\times 10^{-3}$ eV. In contrast, the measured shift of the absorption edge between temperatures above and below the Curie temperature is for EuO $dE_G = -\,2.5\times 10^{-1}$ eV.[1,2] We thus conclude that the shift of the absorption edge due to magnetostriction will be in the direction towards longer wavelengths as suggested by Callen, however, the size of the effect is at least one order of magnitude too small considering the uncertainty in $\mathcal{H}$. As stated above several authors assume the 4*f*–5*d* transition to be responsible for the absorption near the absorption edge. The wave functions of the 5*d*-states overlap and form an empty conduction band, however the 4*f*-wave functions do not overlap and form localized states with no conduction possible. In this case the effective mass in these 'valence states' is very large. If we assume according to Fan[16] that the shift of the absorption edge with temperature due to phonon interaction is a function of $m_v\epsilon_v^2$ and equal to $(dE_G/dT)_{\mathrm{ph}}$ we consequently have to assume the defomation potential ϵ_v to be very small. Thus in this model neglecting ϵ_v, the defomation potential of the conduction band ϵ_c would be about $-\,1.9$ eV.

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