"MIRROR" ABSORPTION AND FLUORESCENCE IN ZnTe

R. E. Dietz and D. G. Thomas
Bell Telephone Laboratories, Murray Hill, New Jersey

and

J. J. Hopfield*
University of California, Berkeley, California
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In this Letter we describe the optical properties of a new type of "center" found in ZnTe. The transition occurs approximately 0.4 eV below the band gap energy. The excited state of this center involves one electron and one hole bound to an impurity. The transition is remarkable, because, although most of its oscillator strength is associated with phonon processes which produce a broad spectrum (whose width is ≈50% of the width of typical F-center transitions), it nevertheless exhibits a weak no-phonon part sharp enough for useful Zeeman measurements. Under suitable conditions, the absorption and emission are mirror images of each other about this zero-phonon line. The excited state of this center is significantly split by electron-hole j:j (exchange) coupling. The two excited states introduce two no-phonon lines, one of which is much broader than the other. The temperature dependence of the shape of the broader line in emission clearly shows that this line is homogeneously broadened (in this particular case, lifetime broadened). That homogeneous and inhomogeneous broadening of impurity lines can be readily distinguished in this case (and other analogous cases) should be of use in understanding line broadening in solids.

ZnTe is a direct band gap semiconductor with the zinc-blende structure, which is normally found to be p type. At 4.2°K it has an exciton transition at 2.381 eV. Crystals may be grown from the melt and from the vapor. In certain vapor-grown crystals, particularly those which have been cooled rapidly after growth, at 77°K a broad absorption peak is seen at 2.10 eV. At 20°K the peak shows much structure. The crystals also fluoresce and at 20°K the fluorescent peaks "mirror" in energy the absorption peaks with one line common to both spectra. This is illustrated in Fig. 1. The fluorescence may be stimulated by excitation above the band gap energy, but it is far more efficient to use the Hg yellow lines which fall in the absorption region of

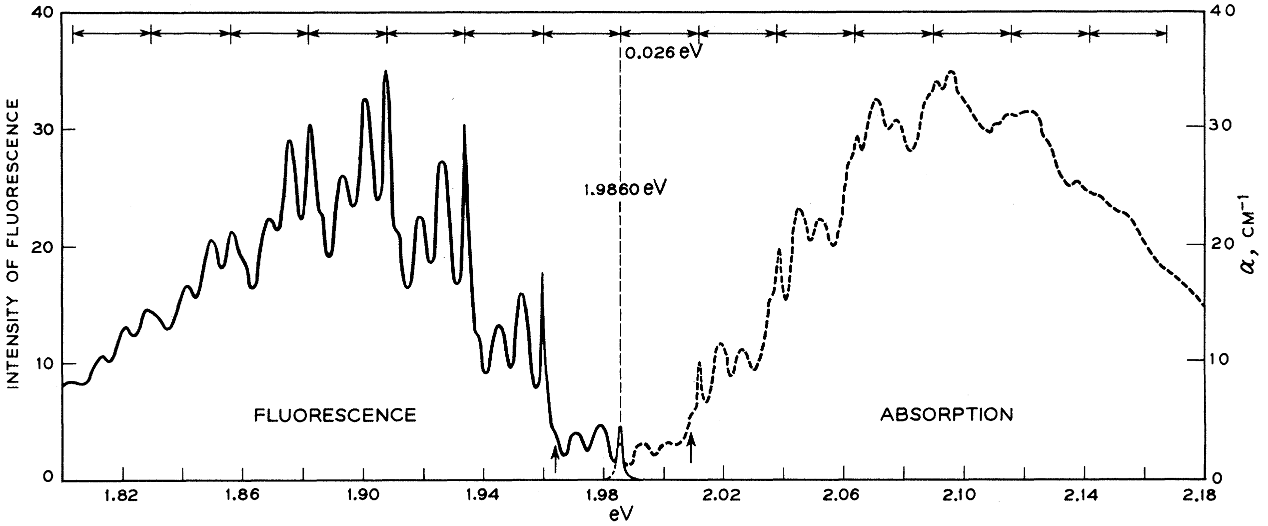

FIG. 1. The fluorescence and absorption at 20°K of the new "center" in ZnTe. The positions of the peaks are "mirrored" about a central no-phonon line common to both spectra. These peaks all relate to the allowed $J=1$ transition. The LO phonon energy is indicated and the arrows mark the no-phonon level cooperating with TO phonons. The two broad peaks in each repeated interval are considered to arise from transverse and longitudinal acoustic phonons.

the transition.

Figure 1 shows that the strength of the transition is chiefly associated with phonon emission processes. The central line common to both absorption and fluorescence must be the no-phonon electronic transition. The longitudinal optical phonon energy of 0.026 eV[1] is indicated in Fig. 1. Clearly this energy marks the repeat interval for the structure which becomes more diffuse as more phonons become involved. Other characteristic phonon energies both acoustic and optical are evident. The unusual clarity of this structure is to be ascribed to the rather large coupling parameter (about 8.8 to the optical phonons); in addition, because of the weak piezoelectric effect, the interaction with the acoustic phonons is not overwhelming and so does not unrecognizably broaden the spectrum. The surprising feature of the 20°K spectrum is the unexpectedly large width of the no-phonon line (the full width at half height is about 0.001 eV).

As the temperature is lowered, the absorption spectrum changes very little, but a new set of emission peaks shifted 0.0017 eV to lower energies begins to appear, and completely displaces the higher temperature emission spectrum at 2°K. The no-phonon line of the low-temperature emission spectrum is very sharp, and is accompanied by an acoustic phonon wing. This shift with temperature for the region near the no-phonon lines is shown in Fig. 2. Analogous shifts take place in the phonon wings.

These results show that the excited state of the transition is split by 0.0017 eV, and that the optical transition from the ground state is allowed to the upper level of the excited state, but forbidden to the lower level. Thus no absorption is seen involving the lower level, and emission from this level only occurs when kT is much less than the splitting between the two levels; i.e., only when the excited system spends much more time in the lower than the upper level.

Of all complexes involving three or fewer electrons and holes, only a complex containing one electron and one hole can give rise to state splittings with some optical transitions allowed and others forbidden. We therefore conclude that the excited state consists of a hole and electron, which may be regarded as an exciton, bound to an ionized donor or acceptor. The splitting of this state must arise from an exchange interaction between the hole and electron. The energy of this state will be approximately the band gap energy minus the binding energy of the donor or acceptor involved. Since the latter quantities can be much larger than the exciton binding energy (which is probably less than 0.02 eV in ZnTe), these bound exciton states can be far removed from the intrinsic excitons. Because of the large spin-orbit splitting (~1 eV) of the valence band, there will be $j{:}j$ coupling between the hole ($j=\frac{3}{2}$), and the electron ($j=\frac{1}{2}$). Thus the allowed transition is to the $J=1$ level and the forbidden to the $J=2$ level, the anticipated crystal field splitting of the $J=2$ level being apparently very small. This model is supported by the following observations: (a) In 31 000 gauss the sharp fluorescent line splits into a quintet as expected for a $J=2$ state. (b) Uniaxial compressive stress produces shifts and splittings in accord with the model. (c) The fluorescence at 1.6°K has a lifetime of about 1 μsec, while at 20°K it is at least 10 times shorter, with substantially the same quantum efficiency.

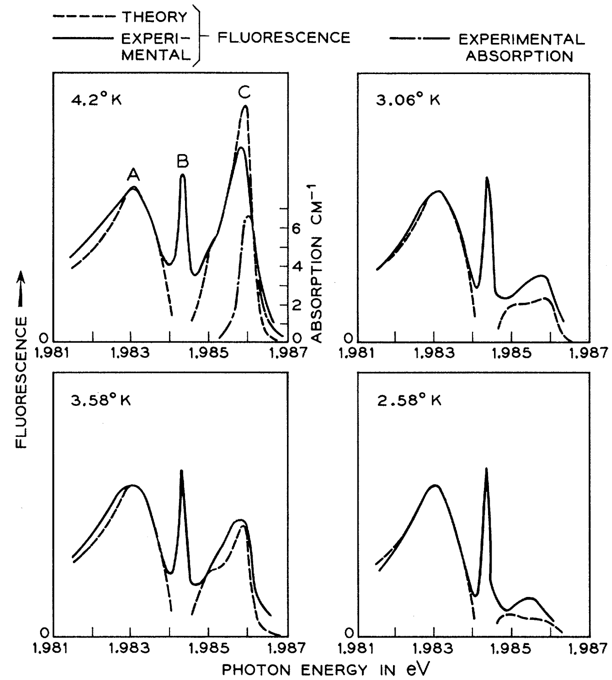

FIG. 2. The fluorescence near the no-phonon lines at several low temperatures. C is the no-phonon $J=1$ line, B is the no-phonon $J=2$ line, and A is an acoustic phonon wing associated with the decay of state B via a virtual phonon transition to state C. As the temperature is lowered, A and B grow at the expense of C. Below 2°K peak C cannot be seen. The absorption at C is shown at 4.2°K; the corresponding fluorescent line is slightly displaced to lower energies. This asymmetry shows that C is homogeneously broadened.

The shapes of the fluorescent and absorption lines in Fig. 2 are determined by acoustic phonons; optical phonons chiefly cause a repetition of the basic pattern as shown in Fig. 1. The $J=1$ state in absorption contains essentially all the oscillator strength and is lifetime broadened by spontaneous phonon emission to the $J=2$ state. In fluorescence, the $J=2$ state can decay in two ways: (1) directly (in a forbidden optical process), producing a sharp optical line, and (2) indirectly, by emitting (or absorbing) an acoustic phonon in a virtual transition to the $J=1$ state, followed by photon emission from the $J=1$ state. The energy of the photon is the energy of the direct transition minus (or plus) the phonon energy. The energy denominator for this second order transition is resonant for the absorption of acoustic phonons having energies near the $J=1$ to $J=2$ state splitting. With this model the shape of the entire emission spectrum of Fig. 2 at low temperatures (below 10°K) can be calculated in perturbation theory from the shape of the low-energy tail of the emission at one temperature and the measured constant width of the absorption line below 10°. These calculations give the theoretical curves of Fig. 2. (The assumption of weak coupling and the neglect of other phonon processes prevent precise agreement with experiment.) That the emission near the position of the $J=1$ symmetrical absorption line must be badly distorted when kT is comparable to the homogeneous linewidth of this state follows from thermodynamic arguments of detailed balance. If this linewidth were due to inhomogeneous effects, such distortion would not occur, as thermal quasi-equilibrium would not be attained.

The precise nature of the center is at present unknown. It seems clear, however, that it is either a compensated donor or acceptor. Annealing treatments in zinc vapor suggest that the center is associated with a stoichiometric defect.

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THERMAL RESISTANCE OF HOLMIUM ETHYL SULFATE*

R. Orbach
Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts

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Recently, Morton and Rosenberg[1] reported the first observation of a change in the thermal conductivity of a paramagnetic salt with the application of an external magnetic field. It is the purpose of this Letter to examine their preliminary results for holmium ethyl sulfate in the light of the present theory of phonon-spin interactions in rare-earth salts, and to indicate some novel aspects of this problem which the theory predicts. We shall show that the peak in the thermal resistance-versus-magnetic field plot displayed in reference 1 is most likely not due to the attenuation of acoustic modes, but rather may be due to the attenuation of a low-level optical mode capable of carrying thermal currents. A second resistance-versus-field peak is predicted, which should fall at the fields predicted for acoustic phonons. Preliminary experimental results support this conclusion.

The thermal conductivity, κ, of a dielectric material is given by[2]

$$\kappa=\tfrac{1}{3}\textstyle\sum_{\vec{f}s}C_{\vec{f}s}v_{\vec{f}s}\Lambda_{\vec{f}s}, \qquad (1)$$

where $\vec{f}$ represents the phonon wave vector; s is the polarization index;

$$C_{\vec{f}s}=[(\hbar\omega)^2/kT]\exp(\hbar\omega/kT)[\exp(\hbar\omega/kT)-1]^{-2},$$

the specific heat per phonon mode; $v_{\vec{f}s}$ is the phonon velocity; and $\Lambda_{\vec{f}s}$ is the phonon mean free path.

For a single phonon interacting with a two-level spin system, it has been shown[3] that

$$1/\Lambda_{\vec{f}s}=1/v_{\vec{f}s}\tau_{\vec{f}s}=(\pi\omega_{\vec{f}s}/\hbar M v_{\vec{f}s}^{\,3})$$
$$\times[\textstyle\sum_m|\langle b|\sum_n V_n^{\,m}|a\rangle|^2]g(\omega_{\vec{f}s}-\omega_s)\Delta N_s, \qquad (2)$$

where $|a\rangle$ and $|b\rangle$ are the two spin states; $V_n^{\,m}$ is a phenomenological spin-phonon coupling constant[4]; and $g(\omega-\omega_s)$ is the spin-phonon line shape function,[5] equal, for a Lorentzian line, to $(T_2/\pi)\times[1+T_2^{\,2}(\omega-\omega_s)^2]^{-1}$. The spin frequency is $\omega_s=\delta_{ab}/\hbar$, δ_{ab} being the energy splitting between the two spin states, and $\Delta N_s=N_a-N_b$, the dif-