PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON THE PHYSICS OF SEMICONDUCTORS, KYOTO, 1966
JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 21, SUPPLEMENT, 1966

IV-2. A Mechanism for Energy Transport by Excitons*

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Detailed consideration of the effects of charged imperfections in solids shows two influences relevant to the question of energy transport associated with excitons. First, such defects create exciton traps, or at least tend to hinder ordinary exciton diffusion. Second, the defects alter the optical absorption in such a way as to provide a new mechanism for energy transport by the photons associated with excitons.

§ 1. Introduction

For a number of years there have been reported observations of energy transport which appeared to be associated with excitons, but which extended over surprisingly long distances. In spite of numerous attempts to explain such transport phenomena, its mechanism still remains unclear. The ordinary diffusion of excitons first proposed, and the ambipolar diffusion of free carriers both are improbable over the distances involved; flourescence effects, while significant, do not by themselves seem to be capable of explaining the observations.[1,2] It is the purpose of the present paper to show that there are additional effects which have not been adequately considered and which have a twofold relevance to this question. These effects may have a substantial influence on exciton diffusion, and may alter the optical properties of a solid in such a way as to provide a new mechanism for energy transport associated with excitons.

The central point of the present work is the recognition of the ways in which natural defects in solids can influence the energy transport processes. Specifically, the electrostatic interaction of an exciton with charged defects is analyzed and shown to have greater magnitude than has generally been realized, thus inhibiting exciton diffusion. In addition, the broadening of the ground state exciton absorption line caused by internal fields of such defects is shown to offer a new possibility for energy transport.

§ 2. Exciton Diffusion

Let us consider a simple Wannier exciton in its ground state. By analogy with the hydrogen atom we find that there is no first order effect of electric field, corresponding to the absence of a permanent dipole moment. Thus the potential energy of an exciton in an electric field F is just

$$V=-\frac{1}{2}\alpha F^2 \tag{1}$$

where α is the exciton polarizability. The negative sign shows this interaction is always attractive, *i.e.*, the exciton is always drawn toward a high-field region, hence toward the defect. The exciton polarizability may readily be evaluated by analogy with the hydrogen atom case:

$$\frac{\alpha}{\alpha_H}=\left(\frac{m}{\mu}\right)\left(\frac{I_H}{I}\right)^2, \tag{2}$$

where α_H and I_H are the polarizability and ionization energy of the hydrogen atom, respectively, μ and I are the reduced mass and ionization energy of the exciton, and m is the free electron mass. The values appropriate for hydrogen are $\alpha_H=(2/3)\times10^{-24}\,\mathrm{cm}^3$ and $I_H=13.6\,\mathrm{eV}$. Since CdS is the material of most interest for the present purposes we use its known values $\mu=0.31m$ and $I=0.027\,\mathrm{eV}$ to get $\alpha=8.2\times10^5\alpha_H$. It is this very large polarizability that warrants the present discussion.[3]

Of the various types of charged defects, one of the most important is the point charge representing an impurity or lattice defect. In the Coulomb field of a point charge in CdS, taking the static dielectric constant as 10.3, the exciton interaction energy becomes

$$V=-\frac{4.9\times10^4}{r^4}\mathrm{eV}, \tag{3}$$

where r is the mean distance between the exciton and the defect measured in Angstrom units. This, of course, is just the potential responsible for the existence of the well-established exciton-impurity complexes or bound excitons. The binding energy of such a complex may be ob-

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* Supported in part by the U. S. Office of Naval Research.

tained from Hopfield's estimate that in CdS it should be 1/10 of the donor impurity ionization energy.[4] Thus an exciton-charged donor complex has a binding energy of $\simeq$.003 eV and from eq. (3), the corresponding diameter is $\simeq$70A. Adding to this the finite size of the exciton itself, we find that such a complex has an effective diameter somewhat over 100 A. Now in the *purest* CdS ($\sim 10^{17}$ impurities/cm^3) the mean separation of impurities is also $\simeq$100 A. It is clear, therefore, that an exciton is rarely free of the influence of an impurity in CdS. Furthermore, since the binding energy of .003 eV corresponds to thermal energy at 35°K, below this temperature excitons should be substantially trapped.

It may be remarked incidentally that these size considerations imply that higher concentrations of impurities would not be favorable for observing such complexes because the interaction of adjacent impurities will distort the Coulomb field necessary to form the complex. It has, indeed, been found that pure crystals are desirable for study of these complexes.[5]

Possibly even more important for exciton transport is the effect of the field in a space charge region near a surface. This is because in transport studies most excitons are produced very close to a surface by using strongly absorbed light. In this case there are no discrete bound states of the type caused by impurities, so estimating the interaction potential depends on knowing the actual field strengths. It is well-known that in equilibrium, surface fields commonly reach values greater than 10^5 V/cm. However, the conditions in which excitons are formed in a transport experiment may be far from equilibrium—there are locally high rates of energy absorption and free carrier generation. If these free carriers do not maintain exact charge neutrality (the Dember effect, for example, would tend to separate them) then they could themselves produce strong local fields just where the excitons are formed by electron-hole pairing. The actual conditions are obviously quite complicated and uncertain, so an assumed field strength of 10^5 V/cm was taken to evaluate the exciton energy. Using this in eq. (1) with the polarizability of CdS we obtain $V \simeq$ .02 eV. This is a very strong effect, corresponding nearly to thermal energy at room temperature. It also happens to be near the ionization energy of the exciton itself so field-induced dissociation would be quite probable.

Thus we see that, in appropriate temperature ranges, both impurities and surfaces can substantially inhibit exciton diffusion. As room temperature is approached, these effects diminish but thermal ionization of the excitons must then occur, also reducing the probability of exciton migration. It should be noted that the hydrogenic model of an exciton in hexagonal CdS may need refinement for these considerations to be applied quantitatively.

§ 3. Exciton Line Broadening and Transport

The second effect of imperfections relevant to the present topic is the alteration of the fundamental optical absorption. It is well known that an interband absorption edge is broadened toward low energies by the Franz-Keldysh effect in the presence of a uniform applied field. In a similar way, it has also been shown that the internal fields of defects cause a low-energy tail to form on the interband absorption edge of imperfect solids in the absence of any externally applied field.[6,7] Very recently the effect of a uniform field on exciton absorption lines was computed.[8] The results indicate that the very narrow, natural line width of an ideal exciton is broadened by the field and a low energy tail is formed just as in the interband case. This is shown pictorially in Fig. 1 in which the absorption coefficient α is plotted *versus* the photon energy $\hbar\omega$ measured from the ideal exciton energy $\hbar\omega_x$ in units of $\hbar\Omega = \hbar(e^2F^2/2\hbar\mu)^{1/3}$ for the case with field. For typical internal field strengths of 10^4-10^5 V/cm the tail extends several hundredths of an electron volt below the ideal exciton line. Thus different regions of a solid have different absorption probabilities in this spectral range determined by the magnitude of the local field strength.

This result can lead to a new mechanism of energy transport in the following manner. The

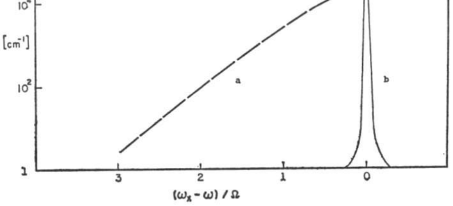

Fig. 1. Exciton absorption with field (a), and without field (b).

surface region at which excitons are generated is considered to be a region of high field. This permits many excitons to have abnormally low energies, *i.e.*, energies in the tail range. It also gives the crystal as a whole an absorption tail due to the surface layers even though the bulk of the crystal may have lower fields and thus be relatively transparent to photons in this spectral range.[7] When the low-energy excitons in the surface region decay radiatively, the emitted photons can be easily transmitted through the bulk to some other high-field surface region where they will be reabsorbed, forming "tail excitons" again. Thus the apparent absorption tail of the crystal does not prevent energy transport by photons of these energies.

As the photons traverse the bulk, of course, they may undergo resonant absorption and emission in the high-field regions near impurities. The extent to which such processes delay, or possibly prevent, the transmission of energy will depend on the lifetime of these intermediate states and their mode of decay. These, in turn, are sensitive to temperature and the exact nature of the defects in the bulk. Thus we have a mechanism by which energy transport can occur, *apparently* by excitons, and with possible delay times in transit.

§ 4. Discussion

This process clearly has some of the features of the fluorescence model of energy transport in that photons carry the energy and defects may play a role in the delay. The chief difference is that the present mechanism involves excitons directly and is capable of producing actual excitons at a distance, in agreement with the recent observations of exciton emission.[2] In the simple form presented here, however, this mechanism is not capable of explaining all of the observations. It may be operative in some temperature ranges but not all.

It appears likely that phonons participate in some energy transport experiments, and within the framework of the present discussion phonons might be included in a generalized definition of defects. This is a somewhat different viewpoint from the customary exciton-phonon interaction which has been treated extensively.[1] In analogy with the foregoing discussion we may consider the longitudinal optic phonons in a polar solid as sources of internal electric fields which could interact with an exciton in the manner of eq. (1). The consequent transport effects would certainly be quite different, however, and will require further consideration.

References

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3) Similar considerations were noted briefly by J. W. Allen: Nature **187** (1960) 51.
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5) D. G. Thomas: private communication.
6) D. Redfield: Phys. Rev. **130** (1963) 916.
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DISCUSSION

Hopfield, J. J.: The field broadening calculated by Duke is due to the fact that continuum electron-hole pair states overlap (in the presence of a uniform electric field) the exciton resonance. The absorption tail represents a final state in which a free electron-hole pair is made via the "exciton" intermediate state. Photoconductivity should exist in this tail. One would believe from this that the absorption and re-emission process you describe would have to be somewhat more complicated.

Redfield D.: When field-induced dissociation of the exciton occurs before it can decay radiatively, then the process would be more complicated and photoconductivity should occur in principle. I am not familiar with any experiment which show such photoconductivity.

Mooser, E.: We have some experimental evidence for the existence of photoconductivity of energies below the gap in GaSe. This evidence would seem to support Hopfield's view.

Green, M. E.: In benzene, where excitons are trapped by a method having nothing to do with an electrostatic field, they are known to be transported from impurity to impurity through the virtual states of the host lattice. I wonder if you could comment on the possibility of this mechanism being important in CdS ?

Redfield, D.: I am not aware of the relevance of such a process to CdS. Perhaps Prof. Toyozawa might comment.

Callaway, J.: In this calculation, and previous ones of a similar type, you apply formulas derived for the case of uniform electric fields to situations in which the electric field has random fluctuations. Would you please indicate over what distance you believe the fields are sensibly constant, and what modifications of your results are produced by the existence of fluctuations.

Redifleld, D.: In the present discussion, the use of the approximation of locally uniform fields is unimportant to the essential conclusions. The existence of strong internal fields is all that is necessary, and that is well-established. As for the use of this approximation in previous calculations, it was found that nearly all of the bulk of a crystal could be described by fields which do not have a substantial fractional variation over distances of the order of several lattice constants. The directional nonuniformity was mentioned in ref. 6).