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ISOELECTRONIC DONORS AND ACCEPTORS

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It is reported that a hitherto unexplained optical transition in ZnTe is due to oxygen substituting isoelectronically for Te. A classification of isoelectronic traps into isoelectronic donors and acceptors is made. One striking difference between these two classes is apparent in the phonon sidebands of the $J=1$ and $J=2$ transitions occuring at each center.

The term isoelectronic trap[1] describes, in a semiconductor, a center which consists of an atom substituting isoelectronically for a host atom, and which will bind a hole and an electron to give a state in the forbidden band gap. Examples recognized so far by the radiative recombination of the bound hole and electron are N[1] or Bi[2] substituting for P in GaP, and Te[3] substituting for S in CdS. This paper reports another isoelectronic trap and shows that for all these traps a classification into isoelectronic donors and acceptors can be made.

In 1962, an extrinsic optical transition of unknown origin in ZnTe was reported[4] which fell 0.4 eV below the band gap. It was found to have two zero-phonon lines A and B ($J=1$ and $J=2$), which arose from the electron ($j=\frac{1}{2}$) and hole ($j=\frac{3}{2}$) coupling. Recently, crystals of ZnTe have been grown using SiO_2, BN, or carbon vessels to contain the molten salt. Runs identical in all respects, save that to one set 5 mole% ZnO was added to the melt, showed that the presence of oxygen increased the concentration of the center, as judged by its absorption spectrum, by at least a factor of 10. Before all measurements the crystals were quenched after equilibrating in 1 atm of Zn at 1000°C. The absence of fine structure in the A, B lines shows that it involves a simple point defect, and it is reasonable to conclude that this is oxygen substituting isoelectronically for tellurium.

Figure 1 shows an over-all view of the tran-

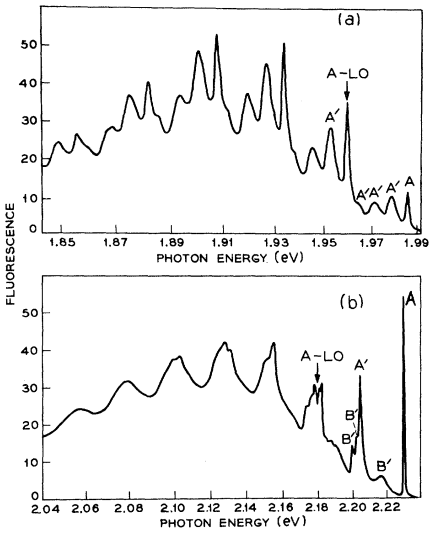

FIG. 1. (a) The fluorescent spectrum of oxygen, an isoelectronic acceptor, in ZnTe at 20°K. A is a zero-phonon line, lifetime broadened by decay of the $J=1$ state to the lower energy $J=2$ state.[4] Some of the phonon replicas of A are marked A'. The LO replica is also indicated. The zero-phonon line falls about 0.4 eV below the band-gap energy of ZnTe. (b) A similiar spectrum for the isoelectronic donor Bi in GaP. An analogous A line, and its phonon wings, is seen. In addition there are phonon wings of the B transition, B', as shown by the temperature variation of the spectrum and comparison with the low-temperature spectrum [Fig. 2(d)]. The zero-phonon line falls 0.1 eV below the band-gap energy of GaP. All spectra are taken using a photomultiplier with S20 response.

sitions due to O in ZnTe, and to Bi in GaP, as seen in fluorescence at 20°K. The lines marked A are known to be zero-phonon lines since they are seen in absorption at the same energy. Both transitions are reasonably deep and both are dominated by phonon side wings, yet there the similarity ends. Figure 2 shows in greater detail the zero-phonon lines and the close-by phonon wings for both transitions at 1.7 and 20°K. At the low temperature both systems are constrained by population effects to decay from the "forbidden" $J=2$, B, state. (The A-B energy differences are quoted in the figure captions.) Note, however, that while ZnTe:O shows a well-defined zero-phonon B line at 1.6°K, this is almost completely absent from the GaP:Bi spectrum. In addition, while the phonon wings of the A and B transitions of ZnTe:O are quite similar to one another, those of A and B of GaP:Bi are quite different. Another difference is that the ratio f_A/f_B, where f_A and f_B are the oscillator strengths of the A and B transitions including the phonon wings, are quite different for the two transitions. An estimate based on the assumption of thermal equilibrium between A and B, and an observation of the ratio of the total light emitted from each state at a certain temperature, shows that f_A/f_B for ZnTe:O is 60, and for GaP:Bi is 7, with an estimated accuracy of a factor of 2. Thus the B transition for GaP:Bi is relatively "more allowed" than it is for ZnTe:O, and the weakness of the zero-phonon line shows that phonon coupling causes the additional oscillator strength. Hence in Fig. 2, at 20°K, GaP:Bi shows a mixture of the A and B transitions and on cooling there is a rapid conversion to the B system, whereas for ZnTe:O at 20°K, only the A system is seen and it is not until 4°K and below is reached that the B component becomes important. Finally, "mirroring" of the absorption and emission spectra about the no-phonon line is found for the ZnTe:O transition.[4] The GaP:Bi absorption spectrum is, however, quite different from the emission spectrum.

There should occur in any semiconductor two kinds of isoelectronic traps. Suppose, for example, a group-IV element having its outer s and p orbitals uniformly lowered by an amount Δ were substituted into silicon. If Δ were large enough, an added electron in the conduction

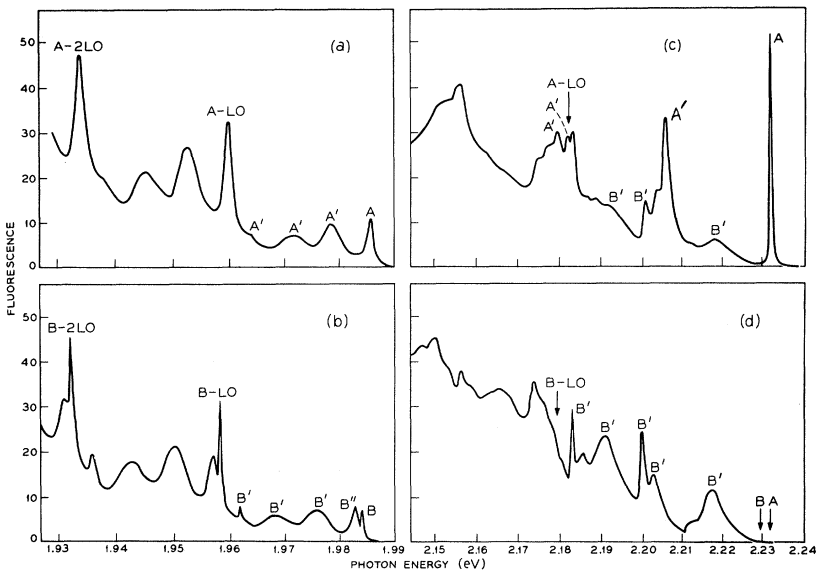

FIG. 2. (a) and (b) The fluorescent spectra on an expanded scale of ZnTe:O at 20 [(a)] and 1.7°K [(b)]. At 20° only the A spectrum is seen and at 1.7° only the B spectrum. Near 4.2°K a mixed spectrum is observed. Apart from the sharpness of B and the extra phonon wing, B'', which is mentioned in the text, the spectra are very similar, being merely shifted by the A-B separation (approximately 1.6 meV). (c) and (d) Similar spectra for GaP:Bi. (c), 20°K; (d), 1.7°K. The A and the B spectra are now quite different. Particularly striking is the observation that the zero-phonon B line is extremely weak compared to its phonon wings. This happens because decay from the B state occurs predominantly via phonon interactions which cross-couple A and B. The A-B separation is 2.7 meV.

band could become bound to this local potential which effectively attracts any electron in its vicinity. It repels holes. If Δ were large and negative, an added conduction electron would be repelled from the site, but a hole could be bound. For the free atom both the electron affinity and ionization potential are proportional to Δ. In GaP, N substituted for P might be an isoelectronic electron trap, and Bi a hole trap; in ZnTe, O substituted for Te an electron trap; and in CdS, Te substituted for S a hole trap. While this description is oversimplified, it should have qualitative validity.

It is interesting to note that all presently known isoelectronic traps are substances of limited solubility in the host crystal. This is reasonable. An isoelectronic substituent will act as a trap if it is sufficiently different from the atom it replaces. This difference, however, makes the substitution energetically unfavorable and so limits the solubility.

If an isoelectronic electron trap has captured an electron, a hole will bind to the long-range Coulomb potential in an acceptorlike wave function. This bound exciton state might be called an isoelectronic acceptor. Similarly, an isoelectronic hole trap will produce an isoelectronic donor, mutatis mutandis. While the electronic energy-level structure of the ground state of isoelectronic donors and acceptors is the same, the phonon coupling can be radically different. The dominant electron-phonon coupling comes from steep spatial gradients in the electron-lattice interactions, which then couple to phonons of large wave vector. Such gradients are caused either by steep gradients in the electron or hole probability density, or the gradient in electron- or hole-phonon coupling in the vicinity of the impurity. It is therefore the particle which is strongly attracted to the local potential which is chiefly responsible for the electron-phonon coupling, so that phonon coupling provides a way of distinguishing between isoelectronic donors and acceptors.

In the absence of spin-orbit coupling, a trapped electron would have symmetry[5] Γ_1, and a trapped hole, symmetry Γ_{15}. For tightly bound particles, a product wave function which is a linear combination of electronic basis functions for Γ_{15} (or Γ_1) times lattice-deformation wave functions is usually a good approximation. In this approximation, the symmetry of lattice distortions which linearly couple to the trapped particles is given by the symmetric products $\Gamma_1 \times \Gamma_1$ or $\Gamma_{15} \times \Gamma_{15}$, namely, for a trapped electron, Γ_1 distortions; for a trapped hole, $\Gamma_1 + \Gamma_{12} + \Gamma_{15}$ distortions. If the spin-orbit splitting is small compared to the band gap, these distortions remain the only important ones. The Γ_1 distortions do not mix different electron (or hole) spin states. The Γ_{12} and Γ_{15} distortions, combined with the spin-orbit coupling in the valence band, provide couplings between the four hole "spin" states.

In the case of the isoelectronic acceptor (electron trap) only Γ_1 phonon couplings will be strong. The lattice cannot then distinguish different electron and hole spin states, and the entire optical emission spectrum from B will be the same as that from A shifted downward by the A-B splitting. The zone-center TO phonon replica should be weak. LO coupling near the zone center is in fact of the Γ_1 variety and will be strong. This description corresponds closely to observations on O in ZnTe. (The B'' peak in Fig. 2 is due to A, B cross-coupling from long-wavelength acoustic phonons interacting with the weakly bound hole[4].) The mirror symmetry of the absorption and emission spectra is also consistent with Γ_1 phonon coupling and the model wave function.

In the case of an isoelectronic donor (trapped hole), coupling to phonons of symmetry Γ_1, Γ_{12}, and Γ_{15} can be strong. Cross-coupling between A and B will now exist through the distortion coupling of different hole "spin" states. If the oscillator strength of the zero-phonon line of B is small, the one-phonon sideband of B will be dominated by those phonons which cross-couple. The intensity of the one-phonon sideband of B will be approximately proportional to the oscillator strength of the zero-phonon line, A, times the A-to-B phonon cross-coupling. The one-phonon sideband of A is approximately proportional to the oscillator strength of A times the A-to-A phonon coupling. The shapes of the phonon sidebands of A and B will now be different. The relative sideband strengths of A and B (at equal population) now being comparable, the zero-phonon line B will appear unusually weak compared to its one-phonon sideband. The total optical decay rates from A and B will be comparable. This description corresponds closely to Bi in GaP. The absence of symmetry between the emission and absorption spectra results from the importance of the Γ_{12} and Γ_{15} phonon coupling.

Although the binding energy of the isoelectron-

ic acceptor N in GaP is too small to correspond closely to the wave function Ansatz used, even for it the one-phonon sidebands qualitatively obey this coupling description, the sidebands of A and B being very similar in form.

In conclusion, it has been shown that oxygen substituting for Te in ZnTe provides a deep isoelectronic trap which is probably very similar to the shallower trap produced by N in GaP. The weak mixing between the A and B states of these transitions can be understood if they are classed as isoelectronic acceptors. On the other hand, the spectrum of the trap due to Bi in GaP reveals strong phonon mixing between the A and B states and shows that this is an isoelectronic donor.

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RADIATION-INDUCED STRUCTURE IN THE dc JOSEPHSON CURRENT*

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We analyze theoretically a method for measuring the temperature dependence of the imaginary part of the gap at the gap edge, $\Delta_2(T)=\Delta_2(\Delta_0(T),T)$, based upon the behavior of the critical dc Josephson current carried by a superconducting tunnel junction in the presence of a high-frequency electromagnetic field. It is shown that the form of this temperature dependence provides a low-frequency probe of the effective electron-phonon coupling.

The superconducting gap parameter, $\Delta(\omega, T)+i\Delta_2(\omega, T)$, is a complex, frequency- and temperature-dependent function. Single-particle electron tunneling experiments,[1] coupled with their theoretical interpretation,[2] have provided detailed information about the frequency structure of Δ at low temperatures. The temperature dependence of this structure has also been investigated.[3,4] In particular, the temperature dependence of $\Delta_0(T)$, the real part of the gap at the gap edge $[\Delta_0(T)=\Delta_1(\Delta_0(T), T)]$, has been carefully measured.[5,6] Here we analyze theoretically a method for measuring the temperature dependence of the imaginary part of the gap at the gap edge, $\Delta_2(T)=\Delta_2(\Delta_0(T), T)$, based upon the behavior of the critical dc Josephson current carried by a superconducting tunnel junction in the presence of a high-frequency electromagnetic field. Using the finite-temperature gap equation,[3] the temperature dependence of $\Delta_2(T)/\Delta_0(T)$ is determined. We point out that the form of this temperature dependence provides a low-frequency probe of the effective electron-phonon coupling.

Because the results and their relationship to the underlying physical processes are probably of more interest than the details of the analysis leading to them, we begin with a discussion of our results.[7] Josephson showed[8] that pairs could tunnel through a thin insulating layer separating two superconductors. This tunneling takes place by means of a virtual intermediate state in which a pair is broken and one partner transferred across the insulator. At zero applied bias, the energy denominator associated with this intermediate state is at least $2\Delta_0$. If, however, there is an applied bias V_0 present, the minimum energy denominator is reduced to $2\Delta_0-eV_0$. Riedel showed that when the bias was such that $eV_0=2\Delta_0$, the overlap of the vanishing energy denominator and the square-root singularities in the single-particle density of states at the gap edge combine to produce a logarithmic singularity in the sum