Further work is in progress on measuring the temperature and field dependence of the magnetic scattering. Three-dimensional data will also be obtained in order to estimate more accurately the conduction electron density, as well as the localized Zr and Zn distributions. These results will be reported in detail elsewhere.

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INTERFERENCE BETWEEN RESONANCE AND POTENTIAL SCATTERING IN uv SPECTRA OF INSULATORS[*]

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Interband optical absorption in crystals may take place with formation of electron-hole pairs in scattering states or in resonant (exciton) states. Because of Van Hove singularities in the interband density of states, structure above the scattering threshold may be due to either process. Difficulties in separating exciton from scattering structure have been encountered in both semiconductors[1,2] and ionic crystals.[3] We note here that these ambiguities can be resolved by utilizing the interference between resonance (exciton) scattering and potential (interband) scattering which is well known in nuclear[4] and atomic physics.[5]

Exciton absorption is represented by a term of the Breit-Wigner form with transition amplitude a_1 and interband scattering by amplitude a_2. The transition rate is proportional to the imaginary part of the dielectric constant

$$\epsilon_2(\omega) \sim |a_1 + a_2|^2, \tag{1}$$

$$a_1 = \frac{i\pi\Gamma}{\hbar\omega - E_0 - E_1 + i\pi\Gamma}. \tag{2}$$

The line width of the Breit-Wigner amplitude (2) is Γ, the unperturbed exciton energy is E_0, and E_1 is the real part of the exciton-scattering self energy.

Interference between a_1 and a_2 can be conveniently discussed using Fano's formulation and notation.[5] Let φ be the unperturbed exciton state, ψ_b the unperturbed band scattering states, and Ψ the eigenstates of the interacting system (including the perturbed exciton state Φ). In terms of the reduced energy variable defined by

$$\epsilon\Gamma/2 = \hbar\omega - E_0 - E_1, \tag{3}$$

the relative transition probability is

$$(q+\epsilon)^2/(1+\epsilon^2). \tag{4}$$

Here q^2 determines the ratio of exciton transitions to unperturbed band transitions. The sign of q determines the asymmetry of the line due to interference effects. It is positive when the interaction is repulsive (nuclear scattering) and negative when, as here, the electron-hole interaction is attractive.[6]

The peak near $\epsilon = 0$ predicted by (4) is asymmetric, with an antiresonant dip below the average absorption rate on the steep side of the peak (see Fig. 1 of reference 5). In principle the interference structure should be observed often for excitons above the scattering threshold. In practice the structure is observed only at temperatures low compared to the Debye temperature. We discuss two cases: CdTe,[2,7,8] shown in Fig. 1(a), and RbI,[9] shown in Fig. 1(b).

The spin-orbit split exciton peaks in CdTe show characteristic asymmetry, sharper on the high-energy side, with shoulders on the low-energy side. Because of spontaneous phonon emission the ideal line shape (which goes to zero in the antiresonance following the sharp edge) is incoherently broadened. Such broadening can be

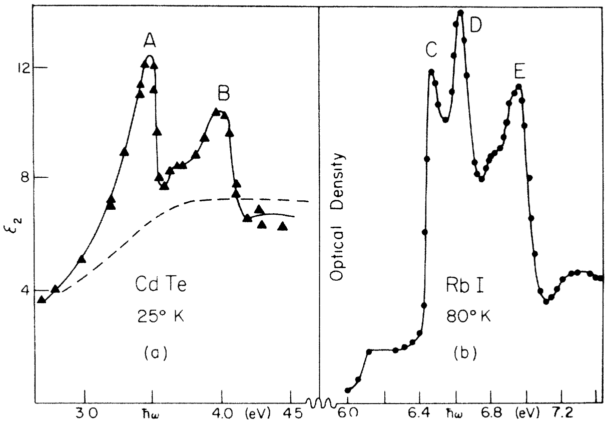

FIG. 1. Asymmetric exciton resonances in (a) CdTe at 25°K; (b) RbI at 80°K. The dashed line in (a) represents a rough estimate of the interband scattering background.

represented by folding the idealized line shape of natural width Γ with a Gaussian of width γ. One can infer Γ/γ from the ratio of peak height above background to dip depth below it, which ratio is about 8 for peak A in CdTe. From Fano's Fig. 3 we obtain a natural width 5 times smaller than the apparent width: $\Gamma/\gamma = 0.2$. The apparent width of peak A is $\gamma = 0.08$ eV, the natural width 0.016 eV. The longitudinal optic phonon energy is 0.02 eV,[10] which justifies the use of Gaussian folding. Because of uncertainties in the interband background level [dashed line in Fig. 1(a)] it is difficult to estimate q, but we guess for peak A that $q = -4.5 \pm 1$.

There are three exciton peaks above the direct threshold in RbI. The first of these is the higher halogen doublet $\Gamma(\frac{1}{2})$ exciton, while the other pair are the spin-orbit split $L(m_J = \frac{3}{2}, \frac{1}{2})$ excitons.[11] All three peaks are asymmetric, the L peaks on the high-energy side and the $\Gamma(\frac{1}{2})$ peak on the low-energy side. The trough at 7.1 eV is probably associated with both a rising interband background and the antiresonance dip of the highest $L(\frac{1}{2}) = E$ exciton. Interference between closely spaced resonance peaks reverses the asymmetry of the lower (higher) peak when the single-peak antiresonance is on the high- (low-) energy side. [This can be shown directly by superposing two amplitudes of the Breit-Wigner form (2).] Thus the proximity of the $L(\frac{3}{2})$ peak to the $\Gamma(\frac{1}{2})$ peak accounts for the reverse asymmetry of the latter. In view of the rapidly varying interband background which includes the $\Gamma_{15}(\frac{1}{2}) \rightarrow \Gamma_1$ threshold between the L exciton peaks, quantitative treatment of the asymmetric line shape does not appear feasible at present.

Using semiconductors one can examine the gradual conversion of a continuum Van Hove edge into an asymmetric exciton resonance. For example, the line shape of the 2-eV edge[2] in Ge is accounted for quite well by continuum absorption alone,[8] while the analogous peaks A and B in CdTe exhibit the characteristic Breit-Wigner form. For this reason it would be of interest to measure ϵ_2 at low temperatures in GaAs near 3 eV and ZnSe near 5 eV by the polarimetric method.[2]

The band structures of the series Ge-GaAs-ZnSe-CdTe are not qualitatively different, but the polaron coupling constant

$$\alpha = (e^2/2\hbar\omega_l)(2m\omega_l/\hbar)^{1/2}(1/\epsilon_\infty - 1/\epsilon_0) \tag{5}$$

varies from 0 (Ge) through 0.2 (GaAs) to 1.1 (ZnSe and CdTe). It has been conjectured[11] that in alkali halides ($\alpha \sim 6$) phonon interaction not only stabilizes the extra exciton resonances but also enhances the binding energy through a Jahn-Teller effect. In general one expects the resonance for increasing α first to become well-defined and then to shift in energy. It appears that there is little energy shift in CdTe. In the alkali halides α is greater by a factor of 5, so that a substantial Jahn-Teller energy shift (0.5 to 0.1 eV) is indicated.

M. H. Cohen adds the following remarks: The case for breakdown of the Franck-Condon principle in the alkali halides can be made stronger. The hole effective masses m_h^* should be used in (5). These increase α more for the alkali halides than for semiconductors such as CdTe. The strongest particle-phonon coupling in the alkali halides occurs for holes with longitudinal acoustic phonons near the (110) edge of the Brillouin zone.[12,13] Call this the homopolaron coupling β. Although β is not directly measurable, it must yield stronger Jahn-Teller effects than α in the alkali halides. Its effect in zincblende crystals, where second neighbor overlap is small, can be neglected. Thus exciton-lattice coupling is dominated by $\alpha \gtrsim 1$ in CdTe and $\beta \gtrsim 20$ in the alkali halides.

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[7] The model of the CdTe structure proposed in reference 2 is equivalent to the assumption that joint density of states for band 4 and band 5 contains accidentally degenerate M_1, M_2, and M_3 Van Hove edges at 3.5 eV. Such a "cutoff" in the interband density of states does not occur for realistic band structures. The nearest approximation to it (which alone could not account for the steep edge near 3.5 eV) is the M_2 Van Hove edge for band 5-band 4 which actually falls at 5.5 eV in CdTe. See reference 8 for a review of interband line shapes in zincblende crystals.

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INTERPRETATION OF EXPERIMENTS ON DISSOCIATIVE ATTACHMENT OR IONIZATION OF MOLECULES*

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The purpose of this Letter is to point out an error in the method normally used to relate the measured kinetic energy of fragment ions to the total energy released in dissociative reactions. In particular, an appreciation of this error leads to an understanding of the discrepancy existing in the literature between the photodetachment measurement[1] of the electron affinity of atomic oxygen, and the value obtained from electron beam experiments in O_2.[2]

In the past, the effect of the thermal motion of the target molecule in a reaction of the type $e + XY \rightarrow X^- + Y$ has been assumed to be negligible. With this assumption, conservation of energy requires that the kinetic energy given to the fragments be $E_R = V_e - (D - A)$. The additional requirement that momentum be conserved leads to the relation[3]

$$E_0 = (1 - \beta)[V_e - (D - A)]. \quad (1)$$

In the above V_e is the electron energy, D is the dissociation energy of XY, A is the electron affinity of the fragment X, E_0 is the kinetic energy of the ion X^-, and $\beta = m/M$ where m is the mass of X^- and M that of the target molecule XY.

The experimental arrangements employed in the study of dissociative processes by electron beams are varied but all methods attempt to determine the ion energy produced by electrons of known energy, by measuring the maximum retarding potential $E_{r\,\max}$ which the ions are able to penetrate. Any apparent spread in ion energies above that expected from the spread in electron energy is ascribed to the ions having entered the retarding field at various angles, it being assumed that the maximum ion energy measured $E_{r\,\max}$ corresponds to the true ion energy, E_0, given by Eq. (1). A linear extrapolation of a plot of $E_{r\,\max}$ vs V_e to zero $E_{r\,\max}$ with a slope determined by Eq. (1) has been interpreted in the past as leading to the proper value of $(D - A)$. It will be shown that this procedure is erroneous, due to the neglect of the thermal motion of the target molecule, leading to a value of A which is likely to be too large.

Theory. —The energy of thermal motion is generally very much smaller than the other terms in the energy equation, and its neglect may be justified on this basis. It may be shown, however, that the random direction of the momentum of thermal motion causes a significant spread in ion energies.

This effect may be understood in terms of the following simple argument. In the absence of thermal motion of the target XY, the ion X^- will have a velocity $v_0 = (2E_0/m)^{1/2}$ where E_0 is given by Eq. (1). If we now assume that all the gas molecules have the same thermal velocity v_T,