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Excitons in semiconducting alloys*

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The physical behavior of excitons in binary semiconducting alloys in strong- and weak-binding limits is discussed. It is pointed out that for weakly bound Wannier excitons, an effective-medium model is more appropriate. The effect of single-particle lifetimes in alloys on the exciton lifetime is discussed. It is suggested that for excitons in $CuBr_xCl_{1-x}$, such single-particle contributions to exciton lifetime are quite significant.

I. INTRODUCTION

Properties of excitons in binary semiconducting alloys like mixed halide crystals or amorphous semiconductors have been of considerable theoretical[1,2] and experimental interest.[3-6] On the experimental side, the important physical properties of the excitons that have been studied for mixed crystals[3] are the concentration dependence of (a) the exciton binding energy, (b) the intensity ratios of excitons associated with the two split valence bands, and (c) the linewidths of excitons. In addition, experiments dealing with the transition from localized to band excitons have been performed.

On the theoretical side, two serious[1,2] attempts have been made. One of these[1] has been to extend the original Frenkel calculation to an amorphous semiconductor. In this method, the eigenvalue equation for the Frenkel exciton is expressed in terms of the radial distribution function for the amorphous system. This method is appropriate for extremely localized excitons and has been utilized to explain qualitatively the properties of excitons in liquid xenon and thin films of boron. The other method has been developed by Sen[2] who has used a two-band coherent-potential approximation[7] (CPA) to explain quite successfully the variation of peak positions of $(p_{3/2}\text{-}s_{1/2})$ and $(p_{1/2}\text{-}s_{1/2})$ excitons (including the effect of exchange mixing) and their intensity ratios (deviation from 2 : 1) with the concentration x for $Cu(Br_xCl_{1-x})$ and $K(Br_xCl_{1-x})$ systems.

In the CPA approach, following an earlier suggestion of Onodera and Toyozawa,[8] Sen starts from a Hamiltonian which consists of two parts. One is a site-diagonal part associated with an exciton localized at that site, and the other is a site-nondiagonal part characterizing the band motion of the exciton. The site-diagonal part of the exciton energy is assumed to vary randomly from site to site for the mixed crystal, whereas the site-nondiagonal part is assumed to be the same for both crystals. The two-band CPA gives an asymmetric Lorentzian line shape for the exciton as seen experimentally. However, the width of the Lorentzian is of the order of 1 meV, which is 10–40 times smaller than that observed experimentally.[3] In addition, the CPA predicts a width which is weakly concentration dependent. Part of this difficulty can be ascribed to the neglect of the phonon contribution to the exciton lifetime. However, we shall show later that there is an intrinsic contribution to the exciton lifetime which is associated with the alloy even in the absence of exciton-phonon interaction. This additional width is expected to be quite important for the mixed crystals.

In this paper, we analyze the nature of the excitons in mixed crystals in two extreme limits, the Frenkel limit and the Wannier limit, and point out an important contribution to the exciton lifetime. This additional lifetime is associated with the single-particle lifetime in alloys and has not been properly accounted for in the CPA formulation. It is also argued that the earlier theoretical models are more appropriate in the Frenkel limit. The behavior of excitons in the other limit, namely, the Wannier limit, which has not been considered earlier will be discussed.

II. EXCITONS IN ALLOYS (PHYSICAL DISCUSSION)

To understand the physical properties of excitons in mixed crystals, we shall for simplicity consider a two-band system, one conduction band and one valence band. This avoids the complications associated with the exchange mixing as observed in mixed halide crystals.[3] It is well known[9] that the exciton state is an N-particle excited state of the crystal (semiconductor) characterized by a binding energy E_B which is essentially the difference in energy of the bound electron-hole pair and the lowest energy of an unbound electron-hole pair. The fundamental energies that are relevant to the understanding of properties of excitons in binary alloys are E_B, the binding energy of the exciton which describes a characteristic internal coherence length r_{ex} of the electron-hole pair, and W, an energy that describes the characteristic fluctuations in the random potential seen by either an electron or a hole. The energy W includes both the strength of the potential difference between the two pure crystals and their degree of admixture as given by x. The two limiting cases that we have pointed out are $E_B \ll W$ and $E_B \gg W$. We shall discuss the two limits separately.

Case 1, $E_B \ll W$. For small E_B, the exciton radius r_{ex} is much larger that l, a characteristic length describing the single-particle mean free path. Under this condition, the electron and the hole can undergo many scatterings independently before interacting with each other. As a result, the exciton is formed out of an effective electron and an effective hole interacting through a Coulomb potential screened by a dielectric constant appropriate to the mixed crystal. We shall refer to this as the effective-medium limit.

Case 2, $E_B \gg W$. For large E_B, r_{ex} is much smaller than l, and the exciton propagates over some distance in the crystal before the electron and the hole get scattered by the potential fluctuation. In this limit, the electron and the hole propagate coherently for a sufficiently long distance before either of these get scattered by the impurity. An appropriate starting point for this limit is a Hamiltonian which is already diagonal in the exciton representation. The effect of the alloy is to mix different exciton states. In this limit the effect of the single-particle lifetime can be taken into account by assuming that the site-diagonal parts of the exciton Hamiltonian is both random and complex and also by going beyond the single-site CPA. The earlier theoretical studies on excitons in mixed crystals and amorphous systems have been carried out in this limit. However, the single-particle lifetime effects have not been incorporated properly into these calculations.

We would like to point out the similarity of the present problem with that of excitons interacting with the longitudinal-optical (LO) polarization field of the periodic lattice.[10] In the latter problem, the two corresponding limits are $E_B \ll \hbar w_{\text{LO}}$, and $E_B \gg \hbar w_{\text{LO}}$, where w_{LO} is the frequency of the LO phonons. In the weak-binding limit ($E_B \ll \hbar w_{\text{LO}}$), one starts from an effective electron and an effective hole, the polarons, which then interact via $-e^2/\epsilon_0 r$ (ϵ_0 is the static dielectric constant) to form the exciton. On the other hand, in the strong-binding case, $E_B \gg \hbar w_{\text{LO}}$, one starts from a bare electron and hole interacting via $-e^2/\epsilon_\infty r$ (ϵ_∞ is the high-frequency dielectric constant) to form an exciton, and then treats the exciton-phonon interaction by perturbation theory. The intermediate case of both problems, $E_B \simeq W$ or $E_B \simeq \hbar w_{\text{LO}}$, is an interesting but difficult theoretical problem and some sort of interpolation procedure[10] developed for the latter (phonon case) case may be useful in the alloy problem.

III. EXCITONS IN ALLOYS (WANNIER LIMIT)

We next consider the two limiting cases separately. For the case of the strong-binding limit, we refer the reader to the work of Sen[2] and Christiaens *et al.*,[1] and consider only the weak-binding limit here. In the weak-binding limit and, in particular, to see how single-particle lifetime contributes to the exciton lifetime, it is desirable to start from a study of the two-particle Green's function appropriate to the alloy system. It is well known that the exciton energy (binding energy and lifetime) is obtained by considering the equation of motion for the two-particle Green's function[9]

$$G_2(12,\, 1'2') = (1/i)^2 \langle T[\psi(1)\psi(2)\psi^\dagger(2')\psi^\dagger(1')]\rangle\,, \tag{1}$$

where $\psi(1)$ refers to the field operator at the space-spin-time point $\vec{r}_1$, ξ_1, and t_1. For the present we confine the calculations to zero temperature for which $\langle\rangle$ refers to the N-particle ground state of the alloy. It should be noted that G_2 refers to an actual alloy and no alloy averaging has been carried out. Since G_2 in Eq. (1) contains information about all possible two-particle excitations (electron-electron, hole-hole, and electron-hole), only one particular time ordering will give the exciton Green's function G_{ex}. This has been discussed by Nozieres,[9] Sham and Rice,[11] and Mahanti and Varma.[10] G_2 can be separated into two parts, i.e.,

$$G_2 = G_{2,f} + G_{2,\text{int}} \tag{2}$$

where $G_{2,f}$ describes a freely propagating electron-hole pair. The exciton energy is obtained by studying the equation of motion of $G_{2,\text{int}}$ or, equivalently, that of the electron-hole scattering matrix[9] $\gamma(k_1k_2k_3k_4)$, where $k_i = \vec{k}_i \zeta_i \sigma_i$ contains momentum, energy, and spin indices.

For a periodic system the total energy, momentum, and spin are conserved in the electron-hole scattering. This leads (disregarding umklapp terms) to

$$\gamma_p(k_1k_2k_3k_4) = \delta(k_1 + k_2 - k_3 - k_4)\tilde{\gamma}_p(k_1k_2k_3k_4)\,, \tag{3}$$

where suffix p refers to the periodic system. On the other hand, for an alloy, although the total energy and total spin are conserved, the total momentum is not. Thus one has

$$\gamma_a(k_1k_2k_3k_4) = \delta(\zeta_1 + \zeta_2 - \zeta_3 - \zeta_4)\delta_{\sigma_1+\sigma_2,\sigma_3+\sigma_4} \times \tilde{\gamma}_a(k_1k_2k_3k_4)\,. \tag{4}$$

From now on we will confine ourselves to the triplet case for which the electron and the hole have opposite spins and ignore the spin indices. The equation of motion of γ_a is given by the Bethe-Salpeter equation[9,12]

$$\gamma_a(k_1k_2k_3k_4) = I_a(k_1k_2k_3k_4) + \sum_{k_5k_6k_7k_8} I_a(k_6k_2k_3k_5)G_e(k_6k_8)G_h(k_5k_7) \times \gamma_a(k_1k_8k_7k_4), \tag{5}$$

which is shown diagrammatically in Fig. 1. G_e and G_h are the electron and hole Green's functions for the alloy. For the alloy G_e and G_h are nondiagonal in momentum indices, i.e.,

$$G_e(k_1k_2) = \delta(\zeta_1 - \zeta_2)\delta_{\sigma_1,\sigma_2}G_e(\vec{k}_1\vec{k}_2, \zeta_1\sigma_1) \tag{6}$$

and a similar equation for $G_h(k_1k_2)$. $I_a(k_1k_2k_3k_4)$ is the irreducible electron-hole interaction for the triplet case. As we have pointed out earlier $\gamma_a(k_1k_2k_3k_4)$ and $I_a(k_1k_2k_3k_4)$ each contains a singular term specifying the energy conservation, i.e., $\delta(\zeta_1 + \zeta_2 - \zeta_3 - \zeta_4)$. We can separate this term by defining $\tilde{\gamma}$ and $\tilde{I}$ through the equation

$$\gamma_a(k_1k_2k_3k_4) = \delta(\zeta_1 + \zeta_2 - \zeta_3 - \zeta_4)\tilde{\gamma}(\vec{k}_i, \zeta\zeta'\omega), \tag{7}$$

where

$$\begin{aligned} &\zeta_2 = \zeta + \omega, \quad \zeta_3 = \zeta, \quad \zeta_4 = \zeta' + \omega, \\ &\zeta_1 = \zeta', \quad \text{and } \vec{k}_i = \vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4, \end{aligned} \tag{8}$$

and an equation similar to (7) for $\tilde{I}$. In Eq. (8) ω is the total electron-hole energy. Since there is no momentum conservation for the random system, $\tilde{\gamma}$ depends upon all the four momenta $\vec{k}_1$, $\vec{k}_2$, $\vec{k}_3$, and $\vec{k}_4$, which we symbolically denote as $\vec{k}_i$. The equation for $\tilde{\gamma}$ is then given by

$$\tilde{\gamma}(\vec{k}_i; \zeta\zeta'\omega) = \tilde{I}(\vec{k}_i; \zeta\zeta'\omega) + \sum_{\vec{k}_5\vec{k}_7,\zeta''} \tilde{I}(\vec{k}_i'; \zeta\zeta''\omega)\tilde{G}_e(\vec{k}_6\vec{k}_8, \zeta'' + \omega) \times \tilde{G}_h(\vec{k}_5\vec{k}_6, \zeta'')\tilde{\gamma}(\vec{k}_i''; \zeta''\zeta'\omega), \tag{9}$$

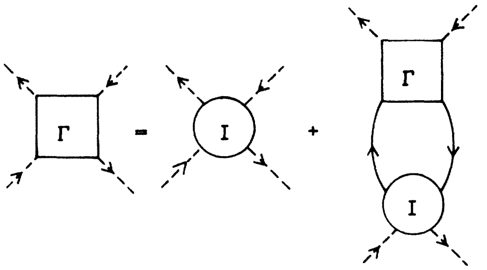

FIG. 1. Bethe-Salpeter equation for the electron-hole scattering matrix in the alloy.

where $\vec{k}_i' = \vec{k}_6, \vec{k}_2, \vec{k}_3, \vec{k}_5$ and $\vec{k}_i'' = \vec{k}_1, \vec{k}_8, \vec{k}_7, \vec{k}_4$. The exciton energy is given by the poles of $\tilde{\gamma}$ in the ω plane, and are given by the solution of the homogeneous Bethe-Salpeter equation,[9] which is obtained from Eq. (9) by dropping $\tilde{I}(\vec{k}_i, \zeta\zeta'\omega)$ from the right-hand side. The homogeneous equation can be symbolically written as

$$\tilde{\gamma} = \tilde{I}\tilde{G}_e\tilde{G}_h\tilde{\gamma}. \tag{10}$$

Next we make the ansatz that the exciton energy for the mixed (random) system is given by the poles of the average $\tilde{\gamma}$, i.e., $\langle\tilde{\gamma}\rangle$, where $\langle\rangle$ refers to the alloy average. This is quite similar to the assumption that the single-particle excitation of the alloy is given by the poles of $\langle G\rangle$, the single-particle Green's function. We can write $\langle\tilde{I}\tilde{G}_e\tilde{G}_h\tilde{\gamma}\rangle$ as

$$\langle\tilde{I}\tilde{G}_e\tilde{G}_h\tilde{\gamma}\rangle = \langle\tilde{I}\rangle\langle\tilde{G}_e\rangle\langle\tilde{G}_h\rangle\langle\tilde{\gamma}\rangle(1 + v), \tag{11}$$

where v incorporates all the vertex corrections introduced by the alloy averaging.[13] The lowest-order approximation which is appropriate in the effective-medium limit is to omit the contribution from v. This leads to a homogeneous Bethe-Salpeter equation for $\langle\tilde{\gamma}\rangle$ given by

$$\langle\tilde{\gamma}\rangle = \langle\tilde{I}\rangle\langle\tilde{G}_e\rangle\langle\tilde{G}_h\rangle\langle\tilde{\gamma}\rangle. \tag{12}$$

The importance of v and its dependence on the exciton energy will be discussed in a future publication. Let's define an average electron-hole scattering matrix Γ by the following equation:

$$\langle\tilde{\gamma}(\vec{k}_1\vec{k}_2\vec{k}_3\vec{k}_4; \zeta\zeta'\omega)\rangle = \Gamma(k, k', Q)\delta(\vec{k}_1 + \vec{k}_2 - \vec{k}_3 - \vec{k}_4), \tag{13}$$

where

$$\begin{aligned} &\vec{k}_2 = \vec{k} + \vec{Q}, \quad \vec{k}_4 = \vec{k}' + \vec{Q}, \quad \vec{k}_3 = \vec{k}, \quad \vec{k}_1 = \vec{k}', \\ &k = \vec{k}\zeta, \quad k' = \vec{k}'\zeta', \quad Q = \vec{Q}\omega. \end{aligned} \tag{14}$$

In addition

$$\langle\tilde{G}(\vec{k}_1\vec{k}_2, \zeta_1)\rangle = G(\vec{k}_1\zeta_1)\delta(\vec{k}_1 - \vec{k}_2). \tag{15}$$

Using equations (12)–(15) we obtain an equation for Γ given by

$$\Gamma(kk'; Q) = \sum_{k''} I(kk'', Q)G_e(k'' + Q) \times G_h(k'')\Gamma(k''k'; Q). \tag{16}$$

This equation is similar to the one for a periodic (uniform) system except that we have averaged I, G_e, and G_h appearing in it.

In Eq. (16), we see that the exciton energy ω depends quite sensitively on the nature of single-particle excitations in the alloy given by G_e and G_h. Since we are interested in obtaining an effective-mass-like equation[10,11] for the Wannier excitons, it is instructive to see how the equation for

Γ leads to an effective-mass equation in the Wannier limit for the periodic crystal. For the periodic case (in the effective-mass approximation)

$$G_e(k)=\frac{1}{\zeta-E_k^e+i\eta},\quad G_h(k)=\frac{1}{\zeta-E_k^h-i\eta},$$

where (17)

$$E_k^e=E_k^e(0)+\frac{\hbar^2k^2}{2m_e},\quad E_k^h=E^h(0)-\frac{\hbar^2k^2}{2m_h},$$

and the irreducible electron-hole interaction I is given by

$$I(k,k'';Q)=\frac{4\pi e^2}{\epsilon_0|\vec{k}-\vec{k}''|^2},$$

where ϵ_0 is the static dielectric constant appropriate to the pure crystal. Substituting for G_e, G_h, and I in Eq. (16) and carrying out the energy (ζ'') integration, one has the usual effective-mass equation[11] for the Wannier exciton:

$$\left(\Delta-\omega+\frac{(\vec{k}+\vec{Q})^2}{2m_e}+\frac{\vec{k}^2}{2m_h}\right)A(\vec{k},Q)=\sum_{\vec{k}'}\frac{4\pi e^2}{\epsilon_0|\vec{k}-\vec{k}'|^2}A(\vec{k}',Q), \tag{18}$$

where

$$A(k,Q)=\frac{1}{\Delta-\omega+(\vec{k}+\vec{Q})^2/2m_e+\vec{k}^2/2m_h}\Gamma(k,k';Q)$$

and $\Delta=E^e(0)-E^h(0)$ is the single-particle gap. We have suppressed the k' index which appears simply as a parameter in Eq. (16). It is clear from the above derivation that the validity of an effective-mass equation for the exciton depends crucially on the nature of the single-particle spectrum contained in G_e and G_h.

The detailed nature of G_e and G_h for mixed crystals and their effect on the excitonic excitation of these systems will be discussed in a future publication. For the present we make the simplest approximation to G_e, G_h, and I for the alloy and see what are the predictions of the effective-medium model. We assume[14]

$$G_e(\vec{k}\zeta)=\frac{1}{\zeta-E^e(k)+i\Gamma_e},\quad E^e(\vec{k})=E^e(0)^*+\frac{\hbar^2k^2}{2m_e^*}$$

$$G_h(\vec{k}\zeta)=\frac{1}{\zeta-E^h(k)-i\Gamma_h},\quad E^h(k)=E^h(0)^*-\frac{\hbar^2k^2}{2m_h^*}$$

$$I(kk';Q)=\frac{4\pi e^2}{\epsilon_0^*|k-k'|^2}, \tag{19}$$

where the quantities with asterisks refer to the alloy obtained in an effective-mass approximation. $\Gamma_{e,h}$ are the lifetimes of electrons and holes, assumed to be momentum independent. The effective-mass equation for the mixed crystal (for $\vec{Q}=0$) is given by

$$\left(\Delta^*-\omega+\frac{\hbar k^2}{2\mu^*}+i(\Gamma_e+\Gamma_h)\right)A(\vec{k},\omega)=\sum\frac{4\pi e^2}{\epsilon_0^*|\vec{k}-\vec{k}'|^2}A(\vec{k}',\omega), \tag{20}$$

where Δ^* is the average gap. In this model the lifetime of the exciton is given by $(\Gamma_e+\Gamma_h)^{-1}=\Gamma_{ex}^{-1}$, where Γ_e^{-1} and Γ_h^{-1} are, respectively, the single-particle lifetimes associated with the electron and the hole. This contribution to the exciton lifetime is associated with the loss of internal coherence between the propagating electron-hole pair and is different from the lifetime associated with the scattering of an exciton from one exciton state to another by the impurities. We should like to point out that even though the weak-binding limit is not appropriate for the excitons in mixed-halide crystals, an exciton lifetime associated with the single-particle lifetimes (Γ_{ex}^{-1}) will be important for these systems. We shall later give some evidence of this contribution to the exciton lifetime by analyzing the experimental data of Kato *et al.*[3]

IV. EXCITON BINDING IN EFFECTIVE-MEDIUM LIMIT

In order to see what the effective-medium model predicts regarding the concentration dependence of the exciton binding energy in the mixed crystals, let us consider solution of the Eq. (20) for the case $\Gamma_e=\Gamma_h=0$. The lowest-energy state of the exciton is given by

$$\omega_{ex}=\Delta^*-R\mu^*/\epsilon_0^{*2}, \tag{21}$$

where Δ^* is the mixed-crystal direct gap and R is the Rydberg constant. If we have a mixed crystal of the type CA_xB_{1-x} ($CdTe_xS_{1-x}$), the virtual-crystal model[15] for μ^* and ϵ_0^* gives

$$\begin{aligned}\mu_{(x)}^{*-1}&=x\mu_A^{-1}+(1-x)\mu_B^{-1},\\ \epsilon_{0(x)}^{*-1}&=x\epsilon_{0A}^{-1}+(1-x)\epsilon_{0B}^{-1};\end{aligned} \tag{22}$$

one then has

$$E_B(x)=E_B^*(x)+R\left[\frac{x(1-x)}{x\mu_B+(1-x)\mu_A}\left(\frac{\mu_A}{\epsilon_A}-\frac{\mu_B}{\epsilon_B}\right)^2\right], \tag{23}$$

where

$$\begin{aligned}E_B^*(x)&=R\left(\frac{x\mu_A}{\epsilon_A^2}+\frac{(1-x)\mu_B}{\epsilon_B^2}\right)\\ &=xE_{B,A}+(1-x)E_{B,B}.\end{aligned} \tag{24}$$

$E_B^*(x)$ is the binding energy of the exciton if one makes a virtual-crystal model for the exciton energy directly. We have plotted $E_B(x)$ and $E_B^*(x)$ for the $CdTe_xS_{1-x}$ system in Fig. 2. The effective-

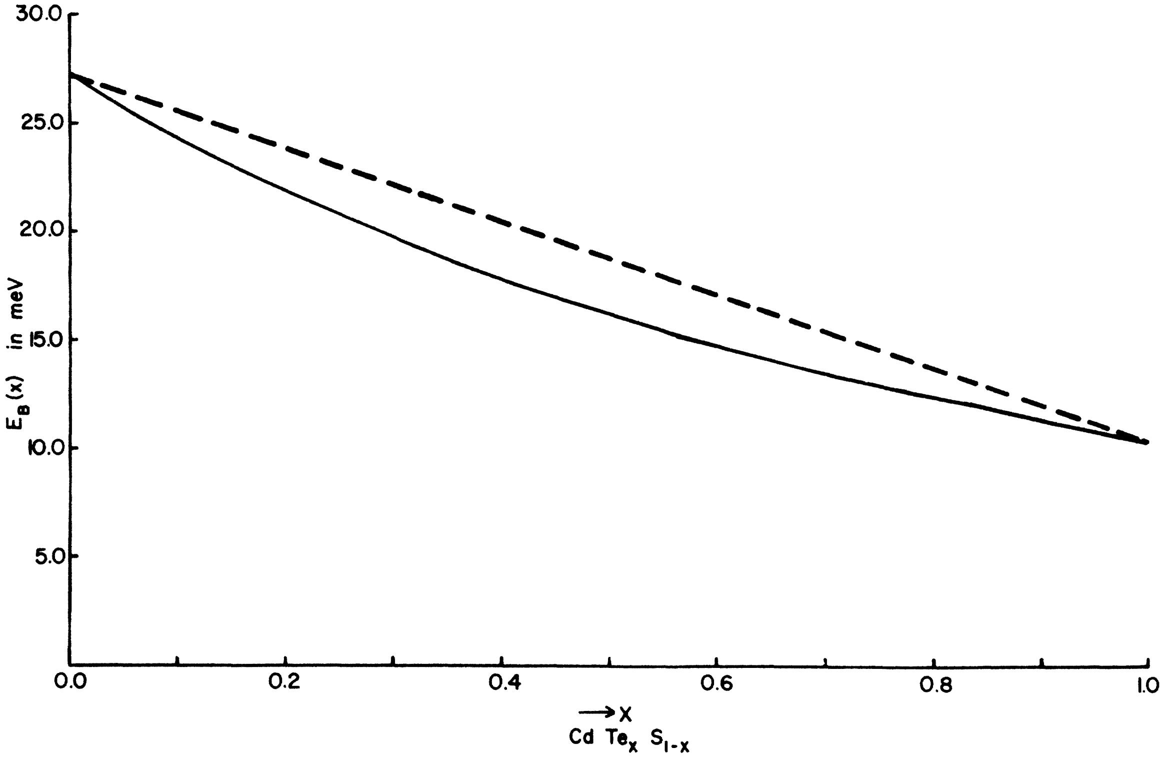

FIG. 2. Exciton binding energy $E_B(x)$ in the effective-medium model (full curve) and virtual-crystal model for the excitons (dotted curve). No experimental values available.

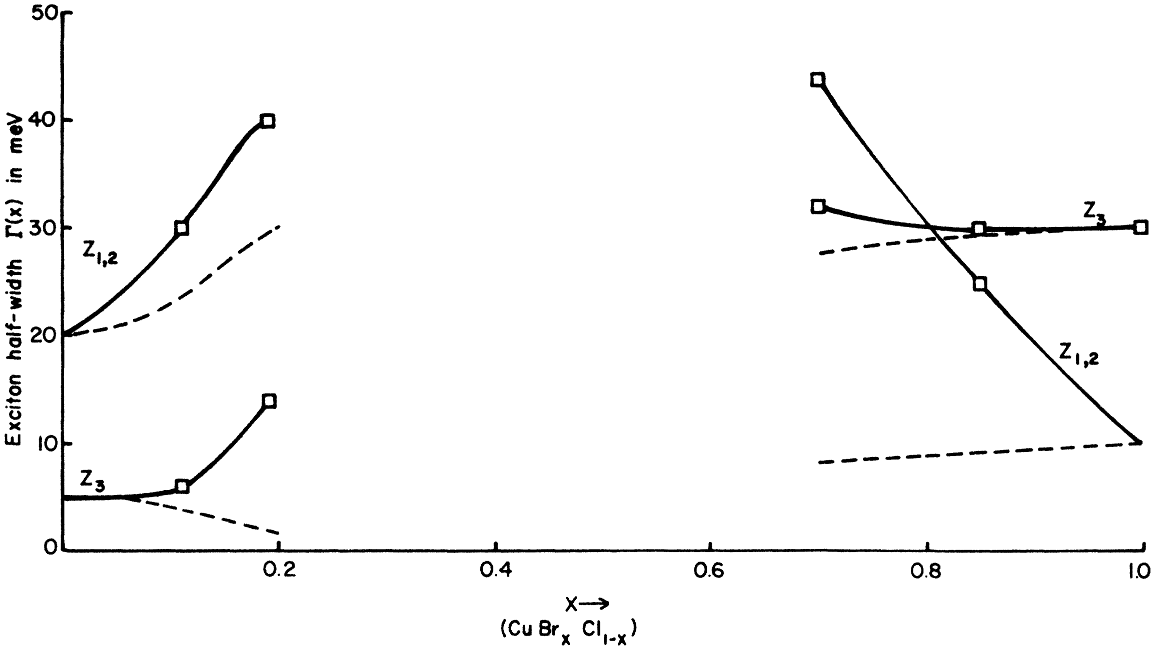

FIG. 3. Experimental and theoretical (virtual-crystal model, see text for explanation) half-widths $\Gamma(x)$ of excitons as a function of alloy concentration for the $CuBr_xCl_{1-x}$ crystals.

medium model with the simplest approximation for the single-particle propagators (virtual-crystal model for G_e, G_h) already predicts significant deviations from the virtual-crystal model for the exciton. The deviation is ~12% for $x = 0.5$. This feature is quite similar to the bowing that one sees in the CPA for excitons.[2] The deviation from the virtual-crystal model for excitons is expected to be quite significant if one uses improved calculations of G_e and G_h, and ϵ_0, which will be discussed in greater detail in a future publication.

V. SINGLE-PARTICLE CONTRIBUTION TO EXCITONS LIFETIME

Next we would like to make some qualitative remarks on the contribution of the single-particle lifetime to the exciton half-width in mixed-halide crystals ($CuCl_xBr_{1-x}$). The CPA calculation of Sen[2] starting from an exciton representation predicts a half-width, Γ_{ex}, of 1 meV, which is nearly x independent and is considerably smaller than the experimental half-width, which is 20–50 meV. Part of this disagreement between theory and experiment could be due to the phonon contribution to the half-width which has been omitted in the CPA calculation. We have plotted in Fig. 3 the experimental half-widths Γ_{expt} of $Z_{1,2}$ and Z_3 excitons for $0 \leqslant x \leqslant 0.2$ and $0.7 \leqslant x \leqslant 1$ taken from the data of Kato *et al.*[3] It is seen that for the pure crystals, the half-widths Γ_{pure} lie between 5 and 30 meV. These linewidths arise primarily from the exciton-phonon interaction. There are some ambiguities in the data at the CuBr end, where the two components of $Z_{1,2}$ exciton are resolved, each having a half-width of 10 meV. But for small concentration of Cl, the two lines are not resolved. In the figure we have used 10 meV for the exciton half-width for the pure CuBr $Z_{1,2}$ exciton.

The contribution to the half-width for the mixed crystals comes from both phonon effects and those associated with the single-particle and other alloy-induced lifetimes. However, it is not possible to separate these lifetimes explicitly. For example, the phonon contributions to the exciton half-width depends upon the energy difference between the two excitons.[16] Since alloying affects this energy difference, it will indirectly affect the phonon-induced lifetimes of the excitons. In addition alloying may specifically alter the phonon spectrum and the nature of exciton-phonon coupling which will result in an alloy-induced change in the phonon contribution to the exciton lifetime. In order to take care of the first effect, we have utilized Toyozawa's model[16] and a virtual-crystal approximation to estimate $\Gamma_{ph}(x)$ and have plotted this in Fig. 3 (dotted lines). At the Cl-rich end where one expects the phonon spectra to be not appreciably modified, $\Gamma_{ph}(x)$ is a reasonable estimate of the phonon-induced lifetime in the alloys. At the Br-rich end, light Cl impurities may give rise to local modes and this is likely to affect exciton-phonon interaction appreciably. In this case $\Gamma_{ph}(x)$ that we have calculated may not be an adequate estimation of the phonon-induced lifetime.

From Fig. 3, comparing the solid lines (Γ_{expt}) and the dotted curves (Γ_{ph}), we see immediately that there is a large additional contribution to Γ_{expt} which cannot be accounted for by Γ_{ph} or by the CPA calculation of Γ_{ex} which is 0 (1 meV). We believe that this additional linewidth is due to the single-particle lifetime that we have mentioned earlier. At the Cl-rich end (for small x), we see that ($\Gamma_{expt} - \Gamma_{ph}$) for $Z_{1,2}$ excitons is larger than that for Z_3 excitons. This is consistent with the fact that the binding energy $E_{B,Z_{1,2}}$ of $Z_{1,2}$ excitons is smaller than E_{B,Z_3}.

In conclusion, we would like to point out that we have shown, although in a qualitative way, the importance of single-particle lifetime effects for excitons in alloys. To be more conclusive, one has to make an improved estimate of $\Gamma_{ph}(x)$, which is presently under study. One would also like to examine the changes in the phonon spectra, particularly at the Br-rich end and see if this can explain the anomalously large broadening of the $Z_{1,2}$ excitons. In addition, a direct quantitative evaluation of the single-particle lifetime contribution will be helpful. Finally we would like to point out that for weakly bound Wannier excitons in semiconducting alloys, an effective-medium-type approach that we have discussed in the text may be more appropriate.[17] Further, the lifetime of excitons may depend quite strongly on the single-particle lifetimes in these alloys. Experimental study to verify this in crystals where Wannier excitons are present will be of considerable help in understanding the nature of weakly bound excitonic excitations in semiconducting alloys.

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[14] This will lead to a symmetric Lorentzian line shape for the spectral weight function $A(\vec{k}, \omega)$ for the single-particle excitations. However, for a semiconductor, the states near the edge may have an asymmetric Lorentzian line shape which will then be reflected in the exciton line shape.

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[17] We should point out that for weakly bound Wannier excitons, there always exists a small x and W for which the exciton representation may also be an adequate starting point. However, in this limit, a virtual-crystal model for the exciton may also be quite adequate, and the difference between the CPA for excitons and the effective-medium model is expected to be small.