

in binary alloys, which supplements (rather than contradicts) the observation of a single sharp cusp in the susceptibility, a macroscopic quantity. It is apparent that the spin system in the alloys becomes localized into finite magnetic clusters whose relaxation times influence the observed physical properties at finite temperatures well before spins can become correlated over an infinite-range scale at a lower or perhaps at zero temperature.

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¹V. Cannella and J. A. Mydosh, Phys. Rev. B **6**, 4220 (1972).

²C. E. Violet and R. J. Borg, Phys. Rev. **149**, 540 (1966); B. Window, G. Longworth, and C. E. Johnson,

J. Phys. C **3**, 2156 (1970).

³K. Adkins and N. Rivier, J. Phys. (Paris), Colloq. **35**, C4-237 (1974); S. F. Edwards and P. W. Anderson, J. Phys. F **5**, 965 (1975); K. H. Fischer, Phys. Rev. Lett. **34**, 1438 (1975); D. Sherrington and B. W. Southern, J. Phys. **5**, L49 (1975).

⁴L. E. Wenger and P. H. Keesom, Phys. Rev. B **11**, 3497 (1975).

⁵V. Cannella, in *Amorphous Magnetism*, edited by H. O. Hooper and A. M. de Graff (Plenum, New York, 1973), pp. 195-206.

⁶L. Néel, C. R. Acad. Sci. **228**, 664 (1949).

⁷A. P. Murani, J. Phys. F **4**, 757 (1974).

⁸D. A. Smith, J. Phys. F **5**, 2148 (1975).

⁹A. P. Murani, S. Roth, P. Radhakrishna, B. D. Rainford, B. R. Coles, K. Ibel, G. Göltz, and F. Mezei, J. Phys. F **6**, 425 (1976).

¹⁰K. Ibel, to be published.

¹¹W. Marshall and R. D. Lowde, Rep. Prog. Phys. **31**, 705 (1968).

¹²M. E. Fisher, J. Math. Phys. (N.Y.) **5**, 944 (1964).

Acceptor Resonances in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}^\dagger$

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Invoking some gross features of the band structure, we show that the resonance energy in the mixed crystal $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ as a zero-gap semiconductor should increase continuously as the molar fraction of CdTe increases. The increase becomes very strong near the point where an energy gap begins to open up in the alloy. This prediction is in qualitative agreement with experiments. We also give comments on two different models for explaining some observed conductivity anomalies.

The localized electronic states in zero-gap semiconductors become resonances because of their interaction with the continuous band states. This problem has attracted considerable attention¹⁻¹¹ especially after evidence for their existence showed up in transport measurements. Some nonmonotonic dependence on temperature in the electronic conductivity was experimentally found⁸⁻¹¹ in HgTe and $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ mixed crystals. For example, in certain samples⁸ of HgTe, anomalous conductivity dips occur around 1 K (A_0), 9 K (A_1), and 32 K (A_2). The A_1 and A_2 anomalies have been interpreted by Finck *et al.*⁸ as due to scattering of conduction electrons by acceptor resonance states associated with mercury vacan-

cies. Since the acceptor state interacts with a conduction band which has a low density of states, it can have sufficiently narrow width to become a true resonance. In spite of the fact that this model has been successful in explaining experimental findings so far,^{7, 8} an alternative has been proposed which interprets the A_2 anomaly as due to resonant scattering by optical phonons.¹² Based only on some gross features of the electronic energy bands, we show in this Letter that the resonance state produced by a short-range potential, as appropriate for vacancies, should undergo a continuous upward shift in energy in mixed crystals of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ as the molar fraction of CdTe is increased from $x=0$ up to the point where the

mixed crystal becomes a normal semiconductor with an energy gap. As an energy gap begins to open up, the resonance state quickly drops into the gap to become a true bound state. Then, its binding energy should increase again with the gap as more CdTe is added. This kind of shift cannot be accounted for by the optical phonon model. As such shifts have already been observed for the resonance state and reported in the literature,⁸ the present work, supplemented perhaps by more detailed data in the future, lends strong support to the acceptor resonance model.

We assume that the vacancy potential couples only three energy bands, the highest two valence bands (Γ_6 and Γ_8 in the zero-gap configuration) and the lowest conduction band (Γ_8). As a generalization of the one-band, one-site model of Koster and Slater,¹³ we use Wannier functions for the three bands centered around the vacancy site as basis to set up 3×3 matrix representations of the one-particle Green's function (real part) G and the vacancy potential V . In doing so, we neglect complications arising from band degeneracies and band crossings, and construct the Wannier functions according to the ordering of the bands at the Γ point. The G matrix so constructed is diagonal and the V matrix is not because of the assumed interband couplings. The position of the resonance state can be located by solving the following determinantal equation:

$$\text{Det}[I - GV] = 0, \quad (1)$$

where I is a unit matrix. Let us label the three bands by $-1, 0, +1$, starting with the lowest. With the assumption

$$V_{ii}V_{jj} \approx |V_{ij}|^2, \quad i, j = -1, 0, +1, \quad (2)$$

we can approximate Eq. (1) by a simpler equation:

$$G_0 + \frac{V_{-1,-1}}{V_{0,0}}G_{-1} + \frac{V_{+1,+1}}{V_{0,0}}G_{+1} = \frac{1}{V_{0,0}}. \quad (3)$$

This is the equation used to determine the resonance energy in different mixed crystals.

The matrix elements of G are related to the density of states N which is normalized to one particle by the following integral:

$$G_i(E) = \int \frac{N_i(E')}{E - E'} dE', \quad i = -1, 0, +1. \quad (4)$$

It is understood that principal value is to be taken for the integral if the energy E should lie inside a band. For all the bands involved, a simple form for N is assumed. Measuring energy from

the top of the band, we represent it by

$$N_i(E) = (2/\pi W_i^2)(-2EW_i - E^2)^{1/2}, \quad (5)$$

$$-2W_i \leq E \leq 0,$$

where W is half of the bandwidth. The assumed density of states is symmetric about the midpoint of the band. Near the band top and the band bottom, it has an energy dependence appropriate for a parabolic edge. With such a simplified form of N , the Green's function can be readily evaluated:

$$G_i(E) = \frac{2}{W_i} \left\{ 1 + \frac{E}{W_i} - \left[\left(\frac{E}{W_i} \right)^2 + 2 \frac{E}{W_i} \right]^{1/2} \right\}, \quad E \geq 0;$$

$$= 2/W_i(1 + E/W_i), \quad -2W_i \leq E \leq 0;$$

$$= \frac{2}{W_i} \left\{ 1 + \frac{E}{W_i} + \left[\left(\frac{E}{W_i} \right)^2 + 2 \frac{E}{W_i} \right]^{1/2} \right\}, \quad (6)$$

$$E \leq -2W_i.$$

The discontinuity in slope usually associated with the Green's function occurs at the band top, $E = 0$, and at the band bottom, $E = -2W_i$.

Now we are ready to apply Eq. (3) to $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$. As is well known, HgTe is a zero-gap semiconductor (also referred to as a semimetal) with its Γ_6 state lying below the degenerate Γ_8 band edge, and hence has a negative value of $E_g \equiv \Gamma_6 - \Gamma_8 \approx -0.3$ eV. On the other hand, CdTe is a semiconductor with a positive gap $E_g \approx 1.6$ eV. In making a mixture of a semimetal with a semiconductor, the gap E_g can be continuously varied between the two quoted values by changing the molar fraction of CdTe, x . In particular, the Γ_6 - Γ_8 crossover point¹⁴ where $E_g = 0$ occurs at $x \approx 0.16$. In applying Eq. (3) to crystals with different x , we assume that E_g is the only varying parameter. As for the potential matrix elements and the widths of the three bands concerned, we assume that they remain the same. Although the structure of the Γ band edge for the -1 and $+1$ bands will be altered as the value of E_g changes, the density of states in the vicinity of the edge is too small to cause any significant change in G_{-1} and G_{+1} . In accordance with this fact, our model Green's function only depends on the gross feature of the band, namely, on its width which is assumed to stay constant in different mixed crystals. As for the constancy of the vacancy potential matrix elements, we find support for this assumption in the calculated charge-density distribution¹⁵ around a cation, which does not show any significant change in different mixed crystals. Then, as the Γ_6 band changes its position, the

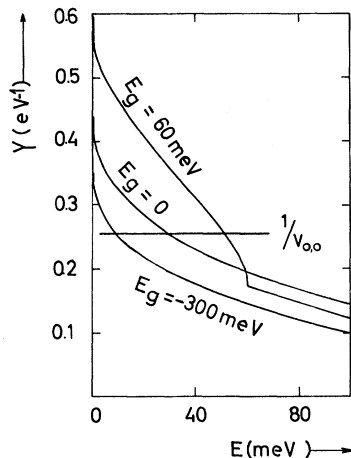


FIG. 1. Figure illustrating the solution of Eq. (3). The left-hand side of this equation is represented by a set of curves, each with a different value of E_g . The right-hand side, $1/V_{0,0}$, has been assigned an arbitrary value for illustration purposes, and is represented by a horizontal line. The energy is measured from the Γ_8 band edge. A discontinuity in slope for curves with a positive E_g occurs at the Γ_8 band edge.

left-hand side of Eq. (3) changes its value at a given energy while its right-hand side remains constant. Hence the solution of this equation has to shift to a different energy. The actual nature of this shift can be seen from a graphical study of Eq. (3) to be discussed below.

To illustrate the solution of Eq. (3), we assign the following representative values to the parameters:

$$W_0 = 2 \text{ eV}, \quad W_{-1} = W_1 = 2.5 \text{ eV},$$

$$V_{-1,-1}/V_{0,0} = 0.3, \quad V_{1,1}/V_{0,0} = 1.$$

By use of Eq. (6), the left-hand side of Eq. (3) can be calculated, and the results are shown in Fig. 1 near and above the Γ_8 band edge where the acceptor resonances occur for some typical values of E_g . The solution of the equation may be obtained by locating the intersecting points of a straight line representing $1/V_{0,0}$ with the various curves. On the semimetallic side, as the Γ_6 state approaches the Γ_8 edge, it increases its contribution to the left-hand side of Eq. (3) at a given energy. Hence, the resonance energy should continuously shift upwards as the magnitude of E_g decreases or, equivalently, as x increases. Immediately beyond the semimetal-semiconductor transition point, the resonance state should decrease its energy slightly relative to the Γ_8 band edge so that it quickly drops into

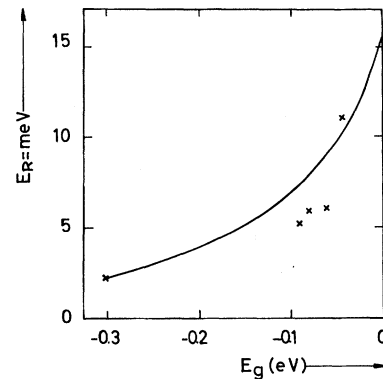


FIG. 2. The calculated A_1 resonance energy (measured from the Γ_8 band edge) as a function of E_g . Experimental points are given as crosses taken from transport measurements (Ref. 8). One experimental point (for HgTe, i.e., $E_g = -0.3$ eV) has been used to obtain the calculated curve.

the gap. Now the acceptor state becomes a true bound state. The binding energy of the localized state begins to increase again as the energy gap is further increased to make it a deep acceptor state. With our choice of parameters and the previously reported position of the A_1 resonance in HgTe at 2.25 meV,⁸ we predict the dependence of the A_1 resonance energy on E_g for the semimetallic configuration and show the results in Fig. 2. We note that the upward shift is much stronger near the semimetal-semiconductor transition point. Some available experimental data are also indicated in the figure. As can be seen, the measured trend of an upward shift of resonance energy agrees with our prediction.

As the calculation of the binding energy of defect states induced by vacancies is known to be a very delicate job even without considering the important lattice-relaxation effects, our highly simplified approach to the problem is susceptible to criticism. However, one must notice that the predicted shift is extremely large; in going from $x = 0$ to $x \approx 0.16$ ($E_g = 0$), there is almost an eight-fold increase in resonance energy according to Fig. 2. Furthermore, this shift only depends on the qualitative behavior of the Green's function. Of all the parameters involved, it is only sensitive to $V_{-1,-1}/V_{0,0}$. Choosing a larger value for this parameter would make the shift stronger. We thus believe that while our quantitative results may not be very meaningful, our qualitative prediction of a strong shift especially near the semimetal-semiconductor transition point is not expected to be altered by any refined calculation.

Let us come back to the optical-phonon model for the A_2 resonance. According to the reported measurements,⁸ the A_2 resonance energy shifts from 9.5 meV for $x=0$ to 21 meV for $x=0.14$. Since as we go from HgTe to CdTe, the optical phonon frequency¹⁶ only changes by about 10%, this model cannot explain the observed large shift. Besides, it has been learned⁸ that whether a clear conductivity anomaly could be seen in a given sample or not depends on the heat treatment of the sample. This indicates that the anomaly is indeed connected with stoichiometric defects rather than with optical phonons. The present work thus lends strong support for the acceptor resonance model. In addition, our predictions about the movement of the acceptor state in the open-gap configuration should induce more experimental investigations in this field.

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¹L. Liu and David Brust, Phys. Rev. **157**, 627 (1967).

²B. L. Gelmont and M. I. Dyakonov, Zh. Eksp. Teor. Fiz. **62**, 713 (1972) [Sov. Phys. JETP **35**, 377 (1972)].

³A. Mauger, S. Otmezguine, C. Vérié, and J. Friedel, in *Proceedings of the Twelfth International Conference on the Physics of Semiconductors, Stuttgart, 1974*, edited by M. Pilkuhn (B. G. Teubner, Stuttgart, Germany, 1974), p. 1166.

⁴G. Bastard, Y. Guldner, A. Mycielski, P. Nozières, and C. Rigaux, in *Proceedings of the Twelfth International Conference on the Physics of Semiconductors, Stuttgart, 1974*, edited by M. Pilkuhn (B. G. Teubner, Stuttgart, Germany, 1974), p. 1162.

⁵A. Mauger and J. Friedel, Phys. Rev. B **12**, 2412 (1975).

⁶G. Bastard and P. Nozières, Phys. Rev. B **13**, 2560, (1976).

⁷L. Liu and C. Vérié, Solid State Commun. (to be published).

⁸C. Finck, S. Otmezguine, G. Weill, and C. Vérié, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Warsaw, 1972*, edited by the Polish Academy of Science (PWN—Polish Scientific Publishers, Warsaw, 1972), p. 944. See this paper for earlier references from this research group.

⁹J. Stankiewicz, W. Giriat, and A. Bienenstock, Phys. Rev. B **4**, 4465 (1971).

¹⁰V. I. Ivanov-Omskii, B. T. Kolomiets, V. K. Ogorodnikov, and K. P. Smekalova, Fiz. Tech. Poluprovodn. **1**, 289 (1967) [Sov. Phys. Semicond. **1**, 232 (1967)].

¹¹J. Stankiewicz and W. Giriat, Phys. Rev. B **13**, 665, (1976).

¹²W. Walukiewicz, Phys. Rev. Lett. **33**, 650 (1974).

¹³G. F. Koster and J. C. Slater, Phys. Rev. **96**, 1208 (1954).

¹⁴C. Vérié, *New Developments in Semiconductors*, edited by P. R. Wallace *et al.* (Noordhoff International Publishing, Leyden, 1972), p. 513.

¹⁵D. J. Chadi and M. L. Cohen, Phys. Rev. B **7**, 692 (1973).

¹⁶A. Mooradian and T. C. Harman, in *Physics of Semimetals and Narrow Gap Semiconductors*, edited by D. L. Carter and R. T. Bate (Pergamon, New York, 1971), p. 297.

COMMENTS

Comment on Higher-Order Nonlinearities and Coupling Saturation of Parametric Decay Instabilities

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The effect of higher-order nonlinearities on the coupling-saturation mechanism for parametric decay instabilities is analyzed. In particular it is shown that cubic nonlinearities in the Poisson equation describing the unstable electrostatic fields play an important role. In the case of the $2\omega_{pe}$ decay instability these effects increase the importance of coupling saturation for $T_e \gg T_i$ and reduce the saturated wave energy by a factor of T_i/T_e .

In a recent Letter¹ we showed that a new nonlinear saturation mechanism for parametric decay instabilities, which we called coupling saturation (CS), arises from cross correlations between Fourier modes. In deriving the equations describing this effect we started from the nonlinear Poisson equation