PHYSICAL REVIEW LETTERS

VOLUME 12 | 9 MARCH 1964 | NUMBER 10

PIEZOELECTRIC POLARON EFFECTS IN CdS†

G. D. Mahan*
Department of Physics, University of California, Berkeley, California
and General Electric Research Laboratory, Schenectady, New York

and

J. J. Hopfield
Department of Physics, University of California, Berkeley, California
(Received 30 January 1964)

Recent cyclotron resonance experiments by Sawamoto,[1] and by Baer and Dexter,[2] measure a conduction mass in CdS significantly smaller than that found by other methods. They get $m_\perp^*=0.177$ and $m_\parallel^*=0.157$, in contrast to $m_\perp^*\approx m_\parallel^*=0.20$ (or 0.19) found by other experiments.[3-7] This Letter is to point out that this difference is explained by considering polaron effects from piezoelectric electron-phonon interactions.

Since the recent discovery that wurtzite-structured semiconductors are vigorously piezoelectric,[8-10] it has become increasingly apparent that many of these low-temperature electronic properties are governed by the piezoelectric electron-phonon interaction—e.g., low-temperature mobility in ZnO and CdS, and phonon drag in ZnO.[8,9]

In piezoelectric crystals, an acoustical phonon has an accompanying electric field proportional to the strain.[11,12] The transverse fields are suppressed to order[13] (speed of sound/speed of light)^2, and the longitudinal electric field in wurtzite gives an electron-phonon interaction

$$\varphi_{\vec{q}}=[4\pi e/\epsilon(\theta)]\{e_{15}\sin\theta(U_{zq}\sin\theta+U_{\perp q}\cos\theta)+e_{31}U_{\perp q}\sin\theta\cos\theta+e_{33}U_{zq}\cos^2\theta\}, \quad (1)$$

$$\epsilon(\theta)=\epsilon_\perp\sin^2\theta+\epsilon_\parallel\cos^2\theta, \quad (2)$$

where $q_z=q\cos\theta$, z is the uniaxial axis; $(U_{\perp q},U_{zq})$ are the components of the phonon displacement amplitude, where $U_{\perp q}$ is in the plane defined by q and z. This form assumes a negligible density of free charge carriers. The presence of other carriers could be included by adding a Debye screening factor.[9] The phonon cloud accompanying an electron (polaron) contributes to the electron self-energy, thereby affecting the effective mass. Since the coupling is weak, this may be calculated by second-order perturbation theory. The angular anisotropy in $\epsilon(\theta)$ and the speed of sound will be ignored, since this is small compared to the anisotropy apparent in the other angular term of (1). The matrix elements are proportional to N_q+1, where N_q is the phonon occupation number, and the induced term N_q is the most important. Even at the experimental temperatures of 1.7°K, the high-temperature expansion of $N_q\approx k_BT/hq$ is valid. Both terms indicated in Fig. 1 were considered and contributed equally. The resulting energy is

$$E(k)=\frac{\hbar^2k^2}{2m_0}-\tfrac{1}{2}\pi\frac{k_BT}{a_Bk}\left[H\left(\frac{k}{k_l}-1\right)\sum_{j=0}^{3}\left(\frac{k_l}{k}\right)^{2j}f_{lj}(\theta)+H\left(\frac{k}{k_s}-1\right)\sum_{j=0}^{3}\left(\frac{k_s}{k}\right)^{2j}f_{sj}(\theta)\right], \quad (3)$$

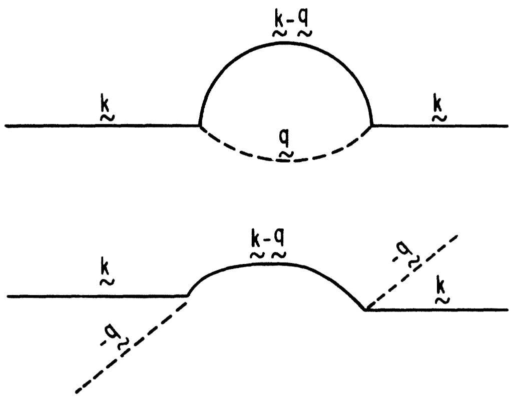

FIG. 1. The two-electron self-energy terms included in the polaron self-energy.

$$f_{\lambda j}(\theta) = \sum_{\alpha=0}^{3} \beta_{\alpha,\lambda} \cos^{2\alpha}\theta, \qquad (4)$$

where m_0 is assumed isotropic, a_B is the Bohr radius, $k = m_0 c_\lambda/\hbar$ for $\lambda = s$ (shear phonons) and $\lambda = l$ (longitudinal phonons), and the step function $H(x)$ is zero for $x < 0$, and one for $x > 0$. In $f_{\lambda j}(\theta)$, the $\beta_{\alpha,\lambda}$ are just combinations of the dimensionless electromechanical coupling constant.[9,14] The self-energy term is quite different from that contributed by deformation potential coupling. The polaron contribution for optical phonons would be of a similar k^{-1} form, but only for those few electrons whose energy exceeds the optical phonon energy of 0.039 eV. The piezoelectric contributions enter for electrons exceeding the speed of sound, which encompasses most of the electrons. Equation (3) must be used to explain the observed anisotropy in the shift from m_0. Attempts to estimate a cyclotron mass have been unsuccessful, due to the complexity of the many terms. That this will account for the observed cyclotron mass measurements may be demonstrated by ignoring the anisotropy, and using an isotropic coupling constant $\alpha = 0.035$ derived by Hutson.[9] When the angular terms of (1) are thereby ignored, the energy is

$$E(k) = \hbar^2 k^2/2m_0 - (\pi k_B T\alpha/2a_B k)H(k/k_s - 1). \qquad (5)$$

This is plotted in Fig. 2 to show the magnitude of the polaron contribution, with $a_B = 24$ Å, $T = 1.7$°K, $m_0 = 0.20$; k_s($c_s = 1.8\times10^5$ cm/sec) was used since shear modes give a dominent contribution to α. The perturbation procedure is not valid for low k, since the calculated shift is larger than the original energy. But since the maximum of a Boltzmann distribution for electrons falls at $k \sim 10k_s$, most electrons are at wave vectors where perturbation theory is valid. The $H(k/k_s - 1)$ factor is dropped since only high k values are of interest. Defining the cyclotron mass as

$$m_c(k)^{-1} = (1/\hbar^2 k)(\partial/\partial k)E(k), \qquad (6)$$

the cyclotron frequency calculated from (5) is

$$\omega_c = \frac{eH}{m_0 c}\left[1 + \frac{\pi}{2}\frac{m_0 k_B T\alpha}{a_B \hbar^2 k^3}\right]. \qquad (7)$$

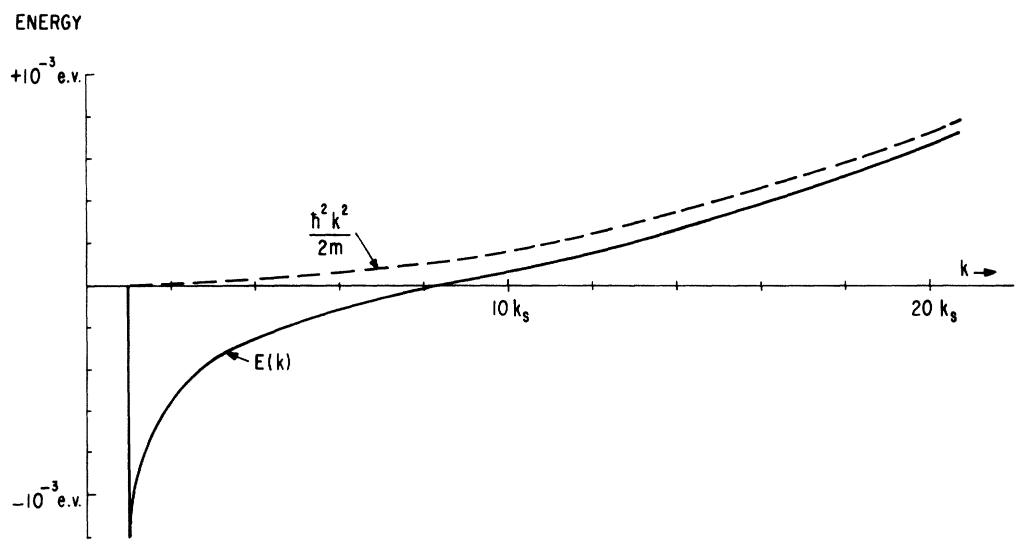

FIG. 2. The effect of the polaron binding upon the electron energy.

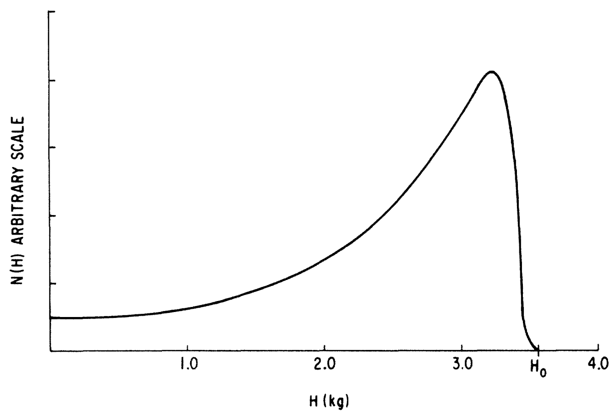

FIG. 3. For a fixed cyclotron frequency, the number of electrons responding to an applied field (for $\tau=\infty$). The observed experimental maximum would be shifted down from H_0, the bare band mass resonance field.

For a fixed frequency, electrons of different wave vectors will respond to different H fields. This may be described to lowest order by assuming the electron distribution to be Boltzmann, and plotting number of electrons against magnetic field, Fig. 3. Using Sawamoto's value of $\omega_c = 49.81$ kMc/sec, the resonant field without polaron contributions is at $H_0 = 3.5$ kG. With polaron effects, the distribution is peaked at 3.2 kG, and has an average of 2.9 kG. As the observed linewidth was 2 kG, the observed maximum would be expected to be between 2.9 and 3.2 kG, in good agreement with Sawamoto's value of 3.0 kG. This demonstrates that the piezoelectric polaron contribution can account for the mass shift.

Equivalent energy shifts would not be observed in other measurements of the conduction mass. The above semiclassical arguments are valid because the experiments are done in weak magnetic fields, where the separation between Landau levels is not much greater than k_BT, and hence the typical acoustical phonon energy. The separation between exciton levels is much greater than k_BT. The Faraday rotation[4] and Hall mobility experiments were run at too high temperatures to see the effect, since at the maximum of the Boltzmann distribution $\hbar^2k^2/2m \sim k_BT$, but the polaron self-energy $\sim T^{1/2}$. Piper and Marple's[5] free-carrier absorption measurements were done at high enough frequencies that acoustical polaron effects would not be important.

An interesting sidelight to the result is the appearance of the dip in the dispersion curve, Fig. 2, for $k \sim k_S$. Although the calculation is not valid in this region, this does suggest that the lowest energy state of an electron in the conduction band is at the speed of sound, and not at $k=0$. This would certainly affect low-temperature mobility and ultrasonic attenuation. Attempts to calculate this behavior in a more self-consistent fashion are in progress.

---

†Research supported by the National Science Foundation.

*Present address: General Electric Research Laboratory, Schenectady, New York.

[1]K. Sawamoto, J. Phys. Soc. Japan 18, 1224 (1963).

[2]W. Baer and R. N. Dexter (private communication); also see footnote of reference 1; R. N. Dexter, J. Phys. Chem. Solids 8, 494 (1959).

[3]J. J. Hopfield and D. G. Thomas, Phys. Rev. 122, 35 (1961).

[4]M. Balkanski and J. J. Hopfield, Physica Status Solidi 2, 632 (1962).

[5]W. W. Piper and D. T. F. Marple, J. Appl. Phys., Suppl. 32, 2237 (1961).

[6]J. D. Zook and R. N. Dexter, Phys. Rev. 129, 1980 (1963).

[7]W. W. Piper and R. E. Halsted, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences, Prague, 1961).

[8]A. R. Hutson, Phys. Rev. Letters 4, 505 (1960).

[9]A. R. Hutson, J. Appl. Phys., Suppl. 32, 2287 (1961).

[10]D. Berlincourt, H. Jaffe, and L. R. Shiozawa, Phys. Rev. 129, 1009 (1963).

[11]H. J. G. Meyer and D. Polder, Physica 19, 255 (1953).

[12]W. A. Harrison, Phys. Rev. 101, 903 (1956).

[13]A. R. Hutson and D. L. White, J. Appl. Phys. 33, 40 (1962).

[14]W. P. Mason, Piezoelectric Crystals and Their Applications to Ultrasonics (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1960).