PHYSICAL REVIEW VOLUME 136, NUMBER 3A 2 NOVEMBER 1964

Electron-Phonon Interaction in Semiconducting Layer Structures

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(Received 8 June 1964)

A new electron-phonon interaction characteristic of layer structures is described. Depending on the strength of the coupling between electron and lattice, this interaction, which involves short-range forces, leads to free or self-trapped charge carriers. The theoretical findings are compared with the experimentally determined charge-carrier mobilities in GaSe and MoS_2.

1. INTRODUCTION

AMONG the known semiconducting compounds, there are a few which crystallize in mica-like layer structures characterized by strong covalent bonds within each layer and by weak van der Waals forces between layers. It will be shown that this marked anisotropy results in a short-range interaction between excess charge carriers and optical lattice vibrations which is specific for layer structures. Similar to the electron-phonon interaction recently discussed by Toyozawa,[1] the present interaction gives rise to the following properties: If the carrier-lattice coupling is weak, the excess carriers behave as free quasiparticles, but if it is strong they become self-trapped in the lattice. The transition between weak and strong coupling is discontinuous and, in the case of weak coupling, theory readily accounts for the anomalously strong temperature dependence of the carrier mobilities observed in GaSe and MoS_2, two semiconductors which both have the mica-like structure envisaged here.

Inspection of the effective potential in which the excess carriers in a layer lattice move reveals the mechanism of the interaction. This potential is reproduced schematically in Fig. 1 for a hypothetical crystal which consists of a series of layers stacked upon each other along the z direction. Within each layer but outside the atomic cores the potential is low and varies slowly. Between the layers, however, the contributions of the different atoms add up to high and fairly wide potential barriers. The carriers may, therefore, be said to move in a series of parallel potential wells in which they have local levels whose energies depend on the local width of the wells. It then follows immediately that the interaction may be described by means of a deformation potential

$$\mathcal{E}_d = a(d\mathcal{E}_1/da)\,, \qquad (1)$$

where $\mathcal{E}_1$ is the energy of the local level and a the width of the well. Approximating the potential within one layer by a deep square well one has

$$\mathcal{E}_1 = n^2\pi^2\hbar^2/2ma^2 \qquad (2)$$

and hence

$$\mathcal{E}_d = -2\mathcal{E}_1. \qquad (3)$$

In the crystals of interest to us, a is of the order of a few angstroms so that even for the lowest level ($n=1$) the deformation potential may be as high as several electron volts. The interaction is, therefore, expected to dominate the transport properties of layer structures and hence to be readily observable in mobility measurements.

2. THE CRYSTAL MODEL

The hypothetical crystal which will serve as basis for our considerations consists of N_z identical layers stacked along the z direction with a primitive vector $\mathbf{d}_z$. Per area S, each of these layers contains N_x unit cells, $\mathbf{d}_x$ being representative of the primitive vectors within the layers. Each unit cell positioned at $\mathbf{n}$ contains a pair of identical atoms (see Fig. 1) which represent an oscillator of reduced mass M, whose only relevant degree of freedom is the deviation ζ_n from the equilibrium interatomic distance a in the z direction.[2] The potential seen by the excess carriers is a superposition of cellular potentials $V(\mathbf{r}-\mathbf{n}, \zeta_n)$ so that the total Hamiltonian takes the form

$$H_{\text{tot}} = H_{\text{el}} + H_{\text{lat}} = -\frac{\hbar^2}{2m}\nabla_r^2 + \sum_n V(\mathbf{r}-\mathbf{n}, \zeta_n) + \sum_n \left[-\frac{\hbar^2}{2M}\nabla^2\zeta_n + \frac{M\omega^2}{2}\zeta_n^2 \right]. \qquad (4)$$

It admits the eigenfunctions

$$\Psi = \sum_n \chi_n(\cdots\zeta_n\cdots)\phi_n(\mathbf{r},\zeta_n)\,, \qquad (5)$$

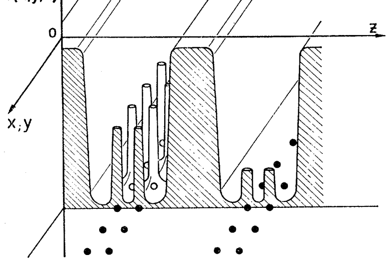

FIG. 1. Schematic representation of the effective potential in a layer structure.

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[1] Y. Toyozawa, *Polarons and Excitons* (Oliver and Boyd, London, 1963).

[2] Vectors occuring as subscripts or superscripts are printed in lightface rather than boldface type.

where the ϕ_n are cellular functions defined by

$$[-(\hbar^2/2m)\nabla_r^2+V(\mathbf{r},\zeta_n)]\phi(\mathbf{n},\zeta_n)=\mathcal{E}(\zeta_n)\phi_n(\mathbf{r},\zeta_n). \quad (6)$$

In this representation the interaction is contained in the ζ_n dependence of the local levels $\mathcal{E}$. The coefficients χ_n of the linear combination (5) satisfy the equation

$$[E-H_{\text{lat}}-\mathcal{E}(\zeta_n)]\chi_n=\sum_d I_{n,n+d}\chi_{n+d}, \quad (7)$$

where E is the total energy and $I_{n,n+d}$ the overlap energy between cell $\mathbf{n}$ and cell $\mathbf{n}+\mathbf{d}$.

At this point we introduce the simplifications justified by the strong anisotropy of the lattice. Thus, we first of all assume the local potential to be separable such that only the z component describing the barrier between the layers depends on ζ_n:

$$V(\mathbf{r},\zeta_n)=V_x(\mathbf{x})+V_z(\mathbf{z},\zeta_n). \quad (8)$$

With this potential, the cellular functions ϕ_n are

$$\phi_n(\mathbf{r},\zeta_n)=\phi_{n_x}(\mathbf{x})\phi_{n_z}(\mathbf{z},\zeta_n), \quad (9)$$

and the corresponding local levels can be expanded as follows:

$$\mathcal{E}=\mathcal{E}_x+\mathcal{E}_z(\zeta_n)=\mathcal{E}_x+\mathcal{E}_z{}^0+(\mathcal{E}_d/a)\zeta_n+\cdots, \quad (10)$$

where $\mathcal{E}_d$ plays the role of a deformation potential. With the expansion (10) and with the normal mode coordinates

$$\zeta_n=\sum_k\left[-i\left(\frac{\hbar}{2MN_xN_z\omega}\right)^{1/2}a_ke^{ikn}+\text{c.c.}\right], \quad (11)$$

a_k and $a_k{}^+$ being the annihilation and creation operators for the phonon state $\mathbf{k}$, Eq. (7) reads

$$\{E-\sum_k[V_ka_ke^{ikn}+\text{c.c.}]-\sum_k\hbar\omega a_k{}^+a_k\}\chi_n =\sum_d I_{n,n+d}\chi_{n+d}, \quad (12)$$

where

$$V_k=-i(\hbar/2MN_xN_z\omega)^{1/2}(\mathcal{E}_d/a). \quad (13)$$

As is specific for interactions of the deformation potential type with optical modes, V_k does not depend on $\mathbf{k}$.

Secondly, the strong anisotropy of the structure suggests that the overlap energies $I_{n,n+d_x}=I_x$ and $I_{n,n+d_z}=I_z$ between adjoining cells satisfy the inequality $I_x\gg I_z$. I_z can therefore be considered as a perturbation, the unperturbed states

$$\Psi_{n_z}{}^0=\phi_{n_z}(\mathbf{z}-\mathbf{n}_z)\sum_{n_x}\chi_{n_x}\phi_{n_x}(\mathbf{x}-\mathbf{n}_x) \quad (14)$$

being confined to a particular layer $\mathbf{n}_z=\text{const}$. If, then, we restrict $\mathbf{k}$ space to the plane $\mathbf{k}_z=0$ which contains the Brillouin zones corresponding to large interlayer distances ($d_z{}^2\gg d_x{}^2$), the $\Psi_{n_z}{}^0$ represents the eigenfunctions of the two-dimensional Hamiltonian

$$H^0=-(\hbar^2\nabla_x{}^2/2m)+\sum_{n_x}V_x(\mathbf{x}-\mathbf{n}_x) +\sum_k[V_ka_ke^{ik_xn_x}+\text{c.c.}]+\sum_k\hbar\omega a_k{}^+a_k, \quad (15)$$

where the $\mathbf{k}_x$ are defined such that within an area S of one layer the functions $e^{ik_xn_x}$ form a complete set. In the effective-mass approximation, (15) takes the form

$$H^0=-(\hbar^2\nabla_x{}^2/2m_x)+\sum_k[V_ka_ke^{ik_xn_x}+\text{c.c.}] +\sum_k\hbar\omega a_k{}^+a_k \quad (16)$$

and we will always assume the effective mass $m_x\approx\hbar^2/2I_xd_x{}^2$ to be isotropic. In conjunction with this Hamiltonian, it is convenient to introduce a dimensionless coupling constant g which contains parameters pertaining only to the properties of a layer:

$$g=(m_xS/4\pi MN_x)^{1/2}(\mathcal{E}_d/a\hbar\omega). \quad (17)$$

3. THE LOW-LYING STATES OF AN EXCESS CARRIER

We are now ready to determine the energy levels of an excess carrier in the model layer structure described above. Omitting the details of calculation we note that the low-lying ones among them can be obtained by minimizing the expectation value[3]

$$E=\langle\chi'|H|\chi'\rangle, \quad (18)$$

where $|\chi'\rangle$ is the trial state

$$|\chi'\rangle=|\Phi(\mathbf{r})\rangle U|0\rangle. \quad (19)$$

$\Phi(\mathbf{r})$ is an electronic function, $|0\rangle$ the phonon vacuum state, and U the unitary transformation

$$U=\exp[\sum_k(f_k{}^*a_k-a_k{}^+f_k)] \quad (20)$$

which has the property

$$U^+a_kU=a_k+f_k. \quad (21)$$

The f_k are the variational parameters representing the displacement of the field oscillators induced by the excess carrier.

If, first of all, we evaluate the unperturbed states which are confined to a single layer, we can in accordance with (14) choose $\Phi(\mathbf{r})$ to be of the form

$$\Phi(\mathbf{r})=\phi_{n_z}(S)^{-1/2}\sum_{n_x}\phi_{n_x}(\mathbf{x}-\mathbf{n}_x)e^{ip_xn_x/\hbar}, \quad (22)$$

which is compatible with the translational symmetry of the layer. The two limiting cases of free and trapped states, which correspond to weak and strong interaction respectively, are then readily obtained, the first with

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[3] E. P. Gross, Ann. Phys. (N. Y.) 8, 78 (1959).

the effective Hamiltonian (16), the second with the exact one (15). The results are:

(*a*) *Weak-Coupling Limit* ($g^2 \ll 1$)

In this case the energy of the excess carrier in the layer is

$$E_f{}^0 = -g^2\hbar\omega \ln(\hbar k^2{}_{\max}/2m_x\omega) + [p_x{}^2/2m_x(1+g^2)], \qquad (23)$$

and corresponds to a free quasiparticle of mass $m_x(1+g^2)$. The unfamiliar form of the self-energy, which contains the maximum wave number $k_{\max}$ in the layer, is due to the fact that $\mathbf{k}$ space is two dimensional.

(*b*) *Strong-Coupling Limit*

Here the energy is

$$E_t{}^0 = -\gamma\hbar\omega - 2I_x e^{-\gamma} \cos(\mathbf{p}_x \cdot \mathbf{d}_x/\hbar), \qquad (24)$$

where the constant $\gamma = \mathcal{E}_d{}^2/2a^2M\omega^2\hbar\omega$ is assumed larger than unity. Corresponding to a narrow conduction band formed with deep-lying states, this spectrum is characteristic of a particle which is self-trapped within a unit cell. Carriers in such states give rise to low-mobility transport phenomena.

It was shown by Toyozawa[1] that for short-range interactions such as the one considered here, the transition from weak- to strong-coupling behavior is discontinuous. By means of the moderately localized wave function,

$$\Phi(\mathbf{r}) = (\alpha/(2\pi)^{\frac{1}{2}}) e^{-\frac{1}{2}\alpha x} \phi(\mathbf{z}), \quad (\alpha^{-2} > d_x{}^2) \qquad (25)$$

one can readily observe this discontinuity. Substituting (25) in (19) and minimizing the expectation value of the Hamiltonian (16) gives

$$E^0 = (\hbar^2\alpha^2/2m_x)(1-2g^2). \qquad (26)$$

The first term of this expression is the energy of localization of the carrier within an area α^{-2} of the layer and the second term is the elastic energy gained from the deformation of the lattice. Minimizing (26) with respect to α leads to the following two alternatives: If $g^2 < \frac{1}{2}$, the energy is positive and tends towards zero as α goes to zero. Because of its negative self-energy the free state is then preferred. If, on the other hand, $g^2 > \frac{1}{2}$, the energy becomes more and more negative as α increases towards its limiting value $\alpha = k_{\max}$ which is imposed by the discrete nature of the lattice. The carrier is then self-trapped within a unit cell.

By comparison the behavior of polarons is entirely different. Unlike the present case where the second term in (26) is proportional to α^2, the elastic energy of a polaron increases linearly with α, so that the corresponding self-energy has a (negative) minimum for $0 < \alpha < k_{\max}$. Moderately localized polaron states are therefore possible and the transition between delocalized and strongly localized states is continuous.

By perturbation calculation we can now construct crystal states in the form of Bloch sums of the unperturbed states, which are invariant with respect to translations $\mathbf{n}_z$. Omitting corrections due to the finite thickness of the phonon Brillouin zones, the corresponding energy spectra for free and self-trapped carriers are

$$E_f = E_f{}^0 - 2I_z(1-g^2)\cos(\mathbf{p}_z \cdot \mathbf{d}_z/\hbar) \qquad (27)$$

and

$$E_t = E_t{}^0 - 2I_z e^{-\gamma} \cos(\mathbf{p}_z \cdot \mathbf{d}_z/\hbar). \qquad (28)$$

4. THE FREE-CARRIER MOBILITY IN LAYER STRUCTURES

Making use of time-dependent perturbation theory we restrict ourselves here to determining the mobility of free carriers to the first order in g^2. For $g^2 \ll \frac{1}{2}$, the low-lying states are described with sufficient accuracy by

$$\Psi = (N_z d_z S)^{-1/2} \sum_n e^{i(p/\hbar)n} \phi_n(\mathbf{r}-\mathbf{n}), \qquad (29)$$

their energy distribution being given by (27). Since I_z is small, we have for all temperatures of interest $I_z < kT$ so that the pertinent part of the spectrum is

$$E \cong p_x{}^2/2m_x. \qquad (30)$$

The corresponding density of states

$$D(E) = \frac{N_z d_z}{2\pi} \frac{S}{4\pi^2} \int_{E=\text{const}} \frac{d\sigma}{\nabla_p E} = \frac{m_x S}{2\pi\hbar^2} N_z \qquad (31)$$

is independent of energy. With (30) and with the perturbation Hamiltonian

$$H_{\text{pert}} = \sum_n [V(\mathbf{r}-\mathbf{n}, \zeta_n) - V(\mathbf{r}-\mathbf{n}, 0)], \qquad (32)$$

the probability of a charge carrier to make a transition from state $\mathbf{p}$ to state $\mathbf{p}'$ while absorbing a phonon with wave vector $\mathbf{k}$ is given by

$$P(\mathbf{p},\mathbf{p}') = \frac{2\pi}{\hbar} \frac{n_k}{N_z S} \frac{\hbar^2}{2m_x} 4\pi g^2 \times \hbar\omega \times \delta(\mathbf{p}-\mathbf{p}'+\mathbf{k}) \delta(E_p - E_{p'} + \hbar\omega), \qquad (33)$$

where n_k is the density of phonons. Since such transitions do not conserve the energy of the carrier, the total scattering probabilities are evaluated by means of the method of Howarth and Sondheimer[4] which leads to the following diagonal components of the mobility tensor:

$$\mu_{xx} = \frac{e}{2m_x\omega} \frac{1}{4\pi g^2} \frac{e^{\hbar\omega/kT}-1}{1+\hbar\omega/2kT}, \qquad (34)$$

$$\mu_{zz} = \mu_{xx} \frac{12 I_z{}^2}{kT\pi^2\hbar^2/2m_x d_z{}^2} \left(1 + \frac{\hbar\omega}{2kT}\right). \qquad (35)$$

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[4] D. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953).

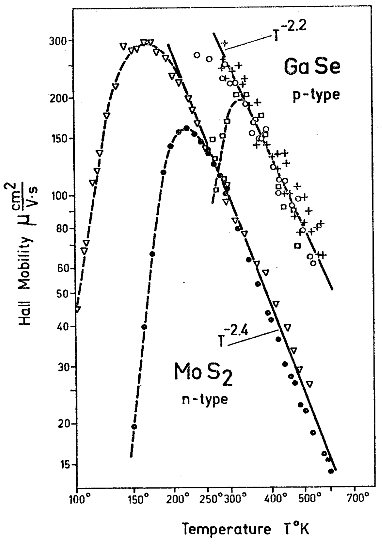

FIG. 2. Hall mobility of the charge carriers in monocrystalline GaSe and MoS_2.

It should be noted that these results are valid only as long as the Boltzmann equation gives the proper distribution of carriers interacting with high-energy phonons.

5. COMPARISON WITH EXPERIMENT AND DISCUSSION

The charge-carrier mobilities of a series of single crystalline samples of p-type GaSe and of n-type MoS_2 are shown in Fig. 2 as functions of temperature. These curves were obtained from four-probe measurements of resistivity and Hall constant[5] with the electric current parallel and the magnetic field perpendicular to the layers. The present room-temperature hole mobility of GaSe is an order of magnitude greater than that reported previously.[6,7] This discrepancy is due to the superior quality of crystals grown from the vapor phase by transport reaction[8] as compared to that of crystals grown from the melt.[9]

The pertinent feature of the experimental findings is the rapid decrease of mobility with increasing temperature.[10] Approximating the high-temperature data by $\mu \sim T^{-\beta}$, one finds β values as high as 2.2 in GaSe and 2.4 in MoS_2, which can be explained in terms of the interaction discussed in the preceding section. Indeed, one arrives at a reasonable agreement between experiment and formula (34) with a vibrational energy 5×10^{-2} eV $< \hbar\omega < 10^{-1}$ eV consistent with the force constants normally met in covalent crystals, with a coupling constant $g^2 \approx 1/40$ corresponding to a deformation potential $\mathcal{E}_d \approx 6$ eV and with an effective mass m_x close to the true electron mass. The over-all consistency of theory reflected by this agreement lends strong support to the proposed interaction between charge carriers and optical phonons in layer structures.

Finally we mention that the crystal model outlined in Sec. 2 affords a simple explanation for the fact that GaSe is always p-type even when heavily doped with Ge, which merely results in a compensation of the excess holes. The argument runs as follows. Valence and conduction bands of a semiconductor are associated with different eigenvalues of the cellular Eq. (6). Since in a layer structure these eigenvalues have the form (10), two nondegenerate ones can differ in $\mathcal{E}_x$ and/or $\mathcal{E}_z$. If, in particular, $\mathcal{E}_z$ is common to both valence and conduction bands, then the deformation potentials for holes and electrons are of the same order of magnitude and the mobilities of the two kinds of carrier are similar. If, however, the $\mathcal{E}_z$ corresponding to the conduction band represents an excited level of the potential well [$n > 1$ in Eq. (2)] then the deformation potential of this band is greater than that of the valence band, which is associated with the lowest level $\mathcal{E}_z$. This immediately leads to the p-type conduction actually observed in GaSe. Moreover, the coupling constant may increase beyond the critical value so that the excess electrons become self-trapped in the manner shown in Sec. 3. It is not unlikely therefore that electron trapping contributes to the formation of the narrow lines found in the absorption edge of GaSe,[6,11,12] which are normally attributed to excitons.[13]

In conclusion we may say that the proposed short-range interaction accounts for some of the properties of semiconducting layer structures and that these structures offer a new field for the experimental confirmation of theories of electron-lattice interaction.

ACKNOWLEDGMENTS

The views expressed in this paper were influenced by frequent discussions with our colleague Dr. J. L. Brebner to whom we extend our gratitude. Thanks are due to R. Béchade and to H. U. Boelsterli for their help in growing the crystals and in carrying out the electrical measurements.

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[10] The ascending low-temperature branches of the mobility curves are related to extrinsic properties and will not, therefore, be considered here.

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