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# Localized lattice instability in zinc-blende semiconductors: Microscopic model for large lattice relaxation and for high-temperature anomalous diamagnetism

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Based on the structural properties of the zinc-blende lattice, a model Hamiltonian is proposed to describe singly and doubly occupied impurity states with large lattice relaxation. One-electron impurity levels are proposed to be connected with the anomalous persistent free-particle excitations. The impurity band of the bound pair states might show Bose condensation and "superconducting" properties at high temperature. Combined with available band-structure data, the metastability and other properties of this model are discussed.

## I. INTRODUCTION

After many unsuccessful experimental attempts[1] and different proposed models[2] on mostly low-dimensional, organic materials, recent magnetic measurements in CuCl (Ref. 3) and CdS (Ref. 4) showed a large diamagnetic anomaly which could be reasonably explained if high-temperature superconductivity were assumed. The excitonic mechanism proposed for the explanation of these phenomena by Abrikosov[5] requires a specific band structure whose existence cannot be proven by the contradicting experimental and theoretical data.[6] Another mechanism has been proposed by Collins *et al.*[7] in which it is assumed that between a triplet pair of electrons (resulting from impurity levels) a condensation as in superfluid $^3$He takes place. The attractive force in this model is provided by the polarization of the electrons in the narrow valence bands in these systems.

In a different type of experiments highly anomalous properties of some deep levels have been recently observed in many semiconducting materials, especially in III-V compounds and mixed crystals of them.[8] Perhaps the most spectacular is the observation of metastable effects such as persistent photoconductivity[9] and photocapacitance quenching[10] accompanied by anomalous photoexcitation and an absorption cross section, and by nonexponential kinetics.

In this paper a new model is proposed which is based on the electrical and structural properties of the zinc-blende lattice and on some specific impurity states. Some elementary microscopic estimations based on this model are capable of describing most of the available, and often seemingly contradictory, experimental facts. Especially, it clarifies somewhat the role of sample preparation in case of the high-temperature anomalous diamagnetism and the very large coupling between the electrons and the lattice. If the model is correct it might also help to design proper preparation methods and some decisive experiments.

## II. DERIVATION OF THE MODEL HAMILTONIAN

The open-structure zinc-blende lattice is inherently unstable at high pressure. Every known zinc-blende semiconductor crystal transforms into a more densely packed structure at high pressure, in the range of 30—150 kbar. Although the detailed atomic mechanism of this transformation has not been yet clarified,[11] it is known that the shear elastic constant $c_s = (c_{11} - c_{12})/2$ and the TA-phonon frequencies along the $\Sigma$ and $\Delta$ lines and at point $X$ are anomalously small and all soften at high pressure. In cubic materials the critical pressure for structural transition and the decrease of the elastic constant $c_s$ are related to each other. This structural stability criterion has been demonstrated for zinc-blende semiconductors.[12]

It is specific in semiconductors with a multivalley indirect conduction band that the elastic constants depend on the electron concentration. Generally the electronic effect changes the shear elastic constant that splits the symmetry degeneracy of the valleys. The change of the shear elastic constant is negative because part of the free energy needed to strain the crystal is recovered by the transfer of electrons from valleys that are raised in energy by the strain to valleys that are lowered. An elementary symmetry argument shows that the electronic effect contributes to $c_s$ in silicon-type materials which have energy minima along the $\Delta$ line, usually at point $X$. The corresponding symmetry-related strain components are $\tilde{\epsilon}_x = (2\epsilon_{xx} - \epsilon_{yy} - \epsilon_{zz})/3$, and by the corresponding change of the indices one can obtain $\tilde{\epsilon}_y$ and $\tilde{\epsilon}_z$, respectively. In the high-strain limit, if the strain has only an $\tilde{\epsilon}_x$ component, the energy at point $X$ in the $\vec{x}$ direction is so much lowered that the repopulation is complete, and hence the energy gain is linearly proportional to the electron density in the lowered minima $(\rho_x = \psi_x^* \psi_x)$ and to the shift of these minima, usually given in units of eV s for unit strain (deformation potential $C_u$). Interestingly enough, this picture is also locally true. A localized impurity wave function can be expressed as a linear combination of the wave functions that form the degenerate minima. If the strain splits the energy degeneracy, the measurable impurity transition energies will also be split (and shifted correspondingly). At high strain the wave function has only components from the minima along the strain.[13]

The proposed model describes impurity electrons which interact with the strain field. If the interaction between electrons and the strain field is strong enough then by spontaneous symmetry breaking in the ground state, the wave function has only components from minima which are lowered by the strain field. If local equilibrium for the strain is assumed then in the adiabatic limit, and when the kinetic energy of the motion of the strained lattice is neglected, the following effective nonlinear Schrödinger equation can be written down for the one-electron impurity states:

$$\left[-\frac{\nabla^2}{2m^*}-\frac{1}{\epsilon_0 r}-C_u s(\rho_x)+f(\rho_x)\right]\psi_x=E_e\psi_x \ . \tag{1}$$

Here the first two terms are the kinetic- and potential-energy terms for a single charged impurity in the effective-mass approximation, and the third term describes the interaction with the (self-induced) strain field. In equilibrium $\tilde{\epsilon}_x=C_u\rho_x/2c_s$. This cannot exceed the critical strain ($\tilde{\epsilon}_x^c$) which causes a transition of the zinc-blende structure. Hence this interaction term should be saturated at a density $\rho_x^c$ (equal to $\tilde{\epsilon}_x^c 2c_s/C_u$). To describe this saturation the following functional form can be proposed for $s(\rho_x)$:

$$s(\rho_x)=C_u(\rho_x^c/c_s)\tanh(\rho_x/\rho_x^c) \ . \tag{2}$$

Here, $c_s$ is determined self-consistently according to the local density (or equivalently according to the local strain). This approximation in the low-strain limit results in the $C_u\rho_x/c_s$ linear interaction term. On the other hand, at high strain it saturates at the proper value. Naturally, in the highly strained (internal) region some contribution from the local "structural change" can be also expected. In lack of detailed microscopic treatment of the problem, however, this additive term is here neglected. The fourth term in Eq. (1) describes the effective electron-electron repulsion in the doubly occupied impurity state, and vanishes for a singly occupied impurity level.

## III. NUMERICAL RESULTS

Equation (1) has to be solved with the condition that the total energy $E_t$ should be minimal. The total energy contains the binding energy of the electron(s), $E_c$, and the energy of the strain field, $E_s$ (equal to $c_s\tilde{\epsilon}^2/2$). With this condition for a singly charged impurity, one-electron and singlet two-electron bound states exist. Here only the ground states which have a spherical symmetry ($s$ state) are investigated. The role of the lattice relaxation in the excited impurity states which are much more delocalized is negligible.

The nonlinear Schrödinger equation [Eq. (1)] can be solved only numerically. Since the deformation $s(\rho_x)$ depends on the electron density, the numerical integration has been done iteratively. The iteration was finished when the relative charge in the density was less than $10^{-3}$ in two consecutive iteration steps. Calculations with more stringent conditions ($10^{-4}$) did not change the relevant energy values more than $10^{-4}$ in relative units. Based on different numerical tests, the estimated accuracy of the numerical results which will be presented in this section is better than 1%.

One-electron solutions are interesting to describe anomalous persistent properties of zinc-blende semiconductors. The detailed discussion of these solutions and a critical comparison with the existing alternative explanations and experimental data will be published elsewhere.[14] Here only some characteristics are listed to illustrate those properties which are relevant also to the two-electron solutions. If some typical material parameters are used for the III-V compounds ($\epsilon_0=10$, $C_u=6$ eV, $c_s=5\times10^{10}$ dyn/cm$^2$, and $m^*=0.35m_e$), the calculated effective Bohr radius is $\sim$25 Å, and the corresponding electrostatic energy is 80 meV, rather similar to the effective hydrogenic value. The elastic distortion is, however, substantial. The range of the "transformed" critical domain is larger than 10 Å, and the total elastic energy is 350 meV. It can be seen that even in a reasonably delocalized impurity state [when the use of the effective Hamiltonian in Eq. (1) can *a posteriori* be justified] an enormous lattice distortion can build up due to the nonlinearity of the electron-lattice interaction and the special "softness" of the zinc-blende structure. In this paper some selected two-electron solutions will be described in some detail. The calculations used the measured or estimated material parameters of CuCl. The effective mass at point $X$ is anisotropic, and the spherical average of $m^*$ is $m^*=0.35m_0$ extrapolated from other zinc-blende materials. This value, with the measured dielectric constant $\epsilon_0=7.9$, gives an effective hydrogen energy of 76.3 meV, which is reasonable for donors at point $X$. Similarly, a typical deformation-potential value of $C_u=6$ eV was taken. The elastic constant and its derivative according to the pressure (up to 5 kbar) have been measured,[15] their values are, respectively, $c_s=4.55\times10^{10}$ dyn/cm$^2$ and $-0.388$. Extrapolation to the first value firmly identified the structural transition of the pure material,[6] giving a limiting value of $c_s^c\approx2\times10^{10}$ dyn/cm$^2$.

There is no measurement for the critical strain $\tilde{\epsilon}_x^c$, but it can be estimated from the limiting value of $c_s^c$ if it is assumed that under an uniaxial stress, the "softening" of the elastic constant $c_s$ is about the same as under hydrostatic conditions. From the measured zinc-blende structural transitions at different stress conditions[11] this is probably an underestimation.

Table I lists the singlet pair-state energies ($E$) at different pressures (at different starting values of $c_s$). The critical strain ($\tilde{\epsilon}_s^c$), the energy of the strain field ($E_s$), and the (thermal) ionization energy of the second electron ($E_{e2}$) are also listed. Owing to the anomalously small value of $c_s$ (Ref. 15), the energy of the lattice deformation in all the investigated cases is larger than the binding energy of an impurity electron in the underformed case. The electron-lattice coupling produces, however, a larger binding energy than this loss, and the binding energy for the second electron is still larger than for the first one if the

TABLE I. Electronic ($E$) and strain energy ($E_s$) of the bound pairs, ionization energy of the second electron ($E_{e2}$), and the critical strain at different pressures.

| Pressure (kbar) | $E$ (meV) | $E_s$ (meV) | $E_{e2}$ (meV) | $\tilde{\epsilon}_x^c$ (%) |
|---|---|---|---|---|
| 0 | $-1865$ | 1196 | $-1112$ | 36.5 |
| 10 | $-1443$ | 957 | $-844$ | 28.2 |
| 20 | $-1030$ | 701 | $-581$ | 20.0 |
| 40 | $-426$ | 271 | $-191$ | $<0.1$ |

strain is larger than about 10%. Similar energy gain was first proposed by Anderson to explain anomalous properties of amorphous silicon.[16] The wave function of the localized pair states has a similar extension as the shallow donor state and the interaction potential both change slowly in the scale of the lattice constant; hence the effective-mass approximation for a first orientation is once again justified.

The theoretically estimated $\Gamma - X$ energy difference in CuCl (which has a direct gap at $\Gamma$) varies between 1.5 and 3 eV, and it is probably larger than the calculated binding energy at all pressures (up to the transition pressure). However, the energy of the free ($\Gamma$) electrons increases near the impurity because of the large strain field. Hence, in a generalized configuration-coordinate diagram[17] an effective energy barrier is expected between the impurity state and the free-electron states. In fact, similarly, large lattice relaxation (LLR) and metastable states have been observed in many zinc-blende III-V and II-VI compounds and in mixed crystals. Since we do not know the exact lattice relaxation around the impurity or the deformation potential for the $\Gamma$ electrons, the barrier height $E_b$ between localized and delocalized states is unknown.

At high impurity densities the wave functions of localized states overlap, and an impurity band arises. If the impurities are ordered in a simple cubic lattice, the bandwidth and the effective mass of the delocalized pair states can be estimated as a function of the density. However, for interacting bosons, Bose condensation may occur. Table II contains the calculated impurity bandwidth, transition temperature $T_c$, and the penetration length $\lambda$ in the simple Bose-condensation model.[18] It is remarkable that at reasonable concentrations the transition temperature turns out to be in the observed range. Calculations with somewhat different material parameters show that the obtained values are rather insensitive for a change of about 50% of these parameters.

## IV. DISCUSSION

A simple effective impurity model Hamiltonian is proposed which includes in a crude way the typical "softness" of the zinc-blende lattice and the resulting anomalously large lattice relaxation. In spirit, this proposition is similar to the polaron concept, but there are, however, significant differences between the two cases. First, the lattice distortion around the impurity cannot be analyzed in a single (optical-phonon) mode, since it arises from shear elastic modes and includes many Fourier components. In addition, the softening of the lattice is crucial, a fact which is not used, as far as the author knows, in the polaron literature. The generalized bipolaron models[19] recently investigated describe only the local change of an electronic state due to an extra electron in some insulating materials. In other words, the types of the bonds are changed at the atom where the extra charge is localized but no occurrence of delocalized lattice distortion (strain) has been postulated. Therefore, these bipolaron states have no common features with the model discussed in this paper.

The solution of the model discussed previously (in Sec. III) is somewhat oversimplified. Hence the numerical data obtained are only indicative. Nevertheless, it is remarkable that many features seem to be in agreement with the following experimental findings (in addition to the high transition temperature which can be obtained, of course, with the aid of many other models).

(1) The calculated pair states are resonant with the estimated positions of the states of the conduction band around the $\Gamma$ point. These pair states are, however,

TABLE II. Calculated impurity bandwidth ($\Delta E$), transition temperature ($T_c$), and penetration length ($\lambda$) for different impurity concentrations and two different pressures ($p$). For columns headed (a), $p=40$ kbar, and for columns headed (b), $p=20$ kbar.

| Concentration ($\times 10^{-19}$ cm$^{-3}$) | $\Delta E$ (meV) (a) | $\Delta E$ (meV) (b) | $T_c$ (k) (a) | $T_c$ (k) (b) | $\lambda$ ($10^{-4}$ cm) (a) | $\lambda$ ($10^{-4}$ cm) (b) |
|---|---|---|---|---|---|---|
| 1.97 | 3.66 | 0.03 | 129 | 10 | 11 | 42 |
| 2.98 | 7.12 | 0.92 | 250 | 33 | 7.7 | 21 |
| 3.76 | 10.06 | 1.91 | 355 | 67 | 6.2 | 14 |
| 4.82 | 14.18 | 4.02 | 501 | 142 | 5.0 | 9.4 |
| 6.34 | 19.82 | 8.21 | 702 | 290 | 4.1 | 6.3 |
| 8.56 | 27.47 | 16.02 | 972 | 567 | 3.3 | 4.3 |
| 11.94 | 38.02 | 29.66 | 1346 | 1050 | 2.6 | 3.0 |

metastable due to the barrier $E_b$ of several tenths of an eV (see above). This explains the inevitable decay of the anomaly, especially by annealing at higher temperatures.

(2) Higher-energy metastable states can only be filled at high temperature (or high pressure), and this, together with the annealing properties, indicates that a reasonable concentration can only be obtained by rapid quenching from the extreme ambient conditions, which are always observed.

(3) Although the structural defects might be important in obtaining an appropriate lattice relaxation around the impurity, in the model proposed the pair states are connected with impurities. This can explain why the effect is so sensitive for the starting material as well as for different materials, that it cannot be reproduced by identical thermal-mechanical routes. It is most interesting—and might further justify this model—that more recently there is some indication that Cl might be related to the anomalous diamagnetism observed in CdS.[4] It has been known for some years that Cl gives rise to an anomalous impurity level with LLR in CdTe and in some related, mixed II-VI compounds.[8] This level is also metastable and can be filled by different temperature and/or pressure routes. The rapid heating and cooling probably provides additional strain.

(4) The optical excitation energy in a state with LLR is much larger than the thermal one (Stokes shift). However, under optical excitation the charge carriers at low temperatures cannot be recaptured[20] by impurities with LLR. If Bose-condensed pair band states exist, they should show special optical properties. Since the one- and two-electron states are well separated and a different LLR is connected with them, the optical excitation energy is higher than the thermal one, quite different from a BCS superconductor material.

(5) In case of CuCl, the LLR with structural defects might enhance the disproportionation reaction—once again, pure samples are more stable than the impure ones.[6]

(6) The coherence length is of the size of the two-electron wave function ($\sim 30$ Å) and it is much smaller than the estimated penetration length ($\sim 10^{-4}$ cm). Hence the proposed condensed state magnetically should behave as a type-II superconductor, in agreement with recent measurements in CdS.[4]

In conclusion, the proposed model may explain some of the anomalous features of the observed high-temperature diamagnetic anomaly. It is tempting to say that the high-conductivity anomaly observed at higher pressure (40 kbar) and room temperature in CuCl[3] has the same origin. Experiments with intentionally doped pure materials should support its validity and supplement other experimental observations.

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