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Temperature Dependence of the Cyclotron Mass of an Electron Polaron in AgBr[†][*]

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We report measurements of the cyclotron effective mass of AgBr as a function of the temperature, which show a temperature dependence given by $m^*(T) = m^*(0) + \mu\exp(-\theta/T)$. The quantities μ and $m^*(0)$ are expressed in units of the free electron mass; μ is sample dependent and on the order of 1, $m^*(0)$ is between 0.286 and 0.289, and the activation temperature θ is ≈80°K. This result can be interpreted as arising from a resonant electron-phonon interaction between an electron in the conduction band of the crystal and a bound impurity state mediated by a LA phonon.

Previous workers[1] have observed that the cyclotron mass of an electron in many ionic crystals (AgBr, AgCl, KCl, KBr, KI, RbCl, RbI) depends on the magnitude of the electric field used in the measurement. In the case of AgBr they estimated the carrier temperature to be ~70°K and assigned the change of mass to the nonparabolicity of the polaron band. The present data, obtained using a superheterodyne spectrometer and optically excited carriers, show instead that these changes are related to an interaction of the carriers with defects rather than to a polaron effect characteristic of a perfect crystal. The same argument developed here to explain the observations in the case of AgBr will explain the anomalously large spin-dependent scattering cross section of carriers by *F* centers in alkali halides.[2] The evaluation of carrier temperatures given in Ref. 1 appears to be an overestimate.

High-purity samples have been used ($\omega\tau > 25$ at 55 GHz and 4°K).[2] The temperature dependence of the mass (Fig. 1) can be described by the expression $m^*(T) = m^*(0) + \mu\exp(-\theta/T)$.

All of the parameters $[m^*(0),\ \mu,\ \text{and}\ \theta]$ depend somewhat on the individual sample and its previous history. When most of the available traps have been saturated with electrons at low temperature, $m^*(0)$ is between $0.286m_0$ and $0.289m_0$, θ is between 70 and 85°K, and μ/m_0 is on the order of 1. Representative data corresponding to two extreme cases are shown in Fig. 1. It is difficult to get a good estimate of the electron mass below ~10°K because the measured mass is a strong function of the applied electric field.

At 4.8°K a noticeable change of the measured cyclotron-resonance mass (Fig. 2) is still observed even when the electric field is changed in the vicinity of 0.3 V/cm. Such changes affect the estimate of $m^*(0)$ that in turn is responsible for larger uncertainties in both μ and θ. Another significant experimental observation is the extreme asymmetry of the cyclotron line at low temperatures (Fig. 3); it becomes broader and more symmetric when the temperature is increased.

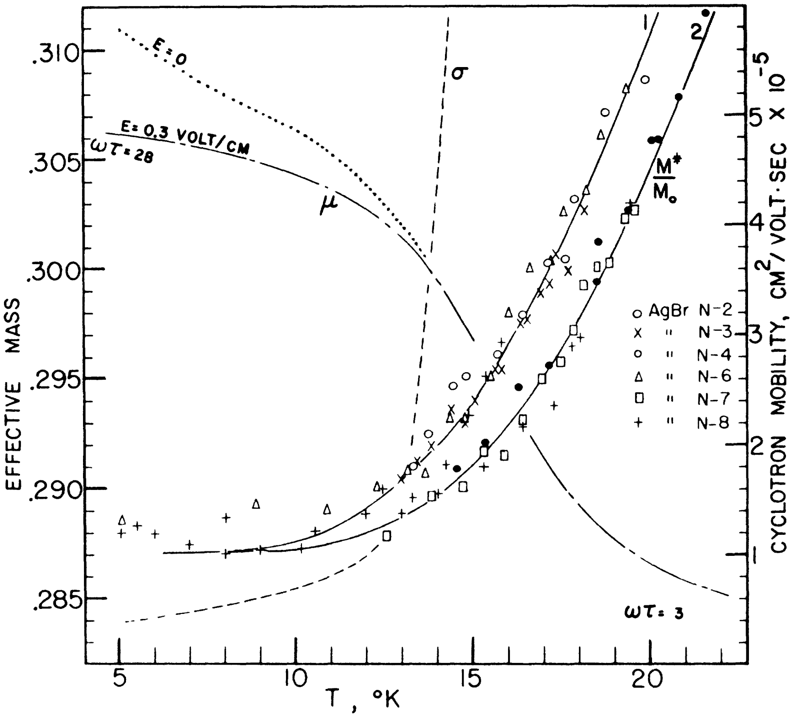

FIG. 1. Temperature dependence of the cyclotron mass m^*/m_0; relative area under the cyclotron absorption, σ (right-hand scale); and cyclotron mobility μ. The dotted line is obtained from the extrapolation to zero microwave field of the microwave field dependence of the cyclotron absorption width. The data shown correspond to samples labeled 2 to 8. Data from other samples lie between curves 1 and 2.

Finally it has been observed that the low-temperature-induced conductivity is predominantly due to holes that contribute a nonresonant background to the rf conductivity. From the temperature dependence of this background signal it is concluded that the hole traps are smaller in number than the electron traps and that the recombination of a free electron and a free hole is more probable than in the case when the former is trapped. The electron traps have been studied

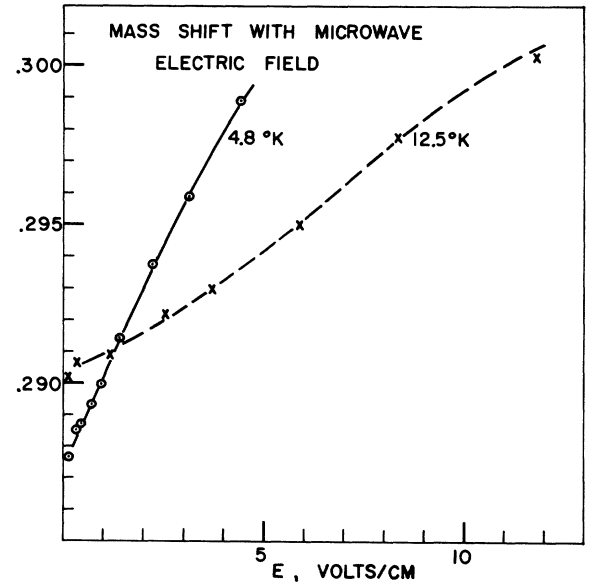

FIG. 2. Dependence of the observed effective mass on the microwave electric field used in the measurement.

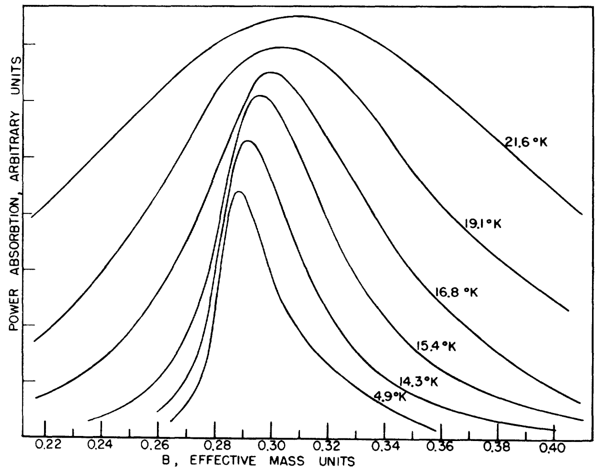

FIG. 3. Shape of the cyclotron resonance absorption as a function of temperature. The scale factors corresponding to different temperatures are not the same.

previously.[3] Their number is on the order of 10^{16} cm^{-3} even in the best samples available. The nature of these traps is unknown. We measured their thermal activation energy (270 ± 30°K) (see Fig. 1); our result is in good agreement with the optical data.[3] Although our ESR sensitivity is 10^{11} spins per cm^3 at 4.2°K for a linewidth of 1 G and an incident microwave power of 10 μW, we were unsuccessful in detecting any ESR signal that could be related to the above traps.

Between 16 and 22°K, $\omega\tau$ has an exponential temperature dependence with an activation energy of 85 ± 30°K (Fig. 1) while at lower temperatures its temperature variation is slower. The observed mobility (34 000 cm^2/V sec at 21°K) is too low to be determined by LO-phonon scattering[4] and its temperature dependence is too rapid to be accounted for by LA phonons.

A study of the indirect optical absorption[5] shows that neither the exciton binding energy nor the self-energy of the electron polaron change with temperature up to at least 45°K implying that the present observation of the changes in effective mass is not an intrinsic property of the perfect crystal.

An estimate of the binding energy of an electron bound in a state corresponding to a quantum number $n = 2$ of a Coulomb center yields[6] ~8 meV, within the framework of the effective-mass approximation. We notice that this energy is close to the observed activation energy of m^* ($6.5 \lesssim \theta \lesssim 7.5$ meV). The predicted $n = 3$ and $n = 4$ states would give rise to induced-optical-absorption lines that coincide with previous observations of Brandt and Brown.[3]

The proximity of the activation energy of m^* and the binding energy of the impurity, the important hot-electron effects observed by us as well as by Hodby,[1] and finally the conclusion that the present observation is not characteristic of a perfect crystal, lead us to search for an explanation related to scattering by impurities.

We visualize such a process as the resonant capture of a conduction-band electron in state $|\vec{k}\rangle$ into a bound state $|b\rangle$ of a charged impurity with the emission of a virtual phonon $|\vec{q}, \mu\rangle$ of wave vector $\vec{q}$ and polarization μ. The bound state is supposed to have energy E_b below the conduction band. The electron is immediately reemitted into state $|\vec{k}\rangle$ with the absorption of the phonon. This effect becomes important when the energy of the phonon, $\hbar\omega$, is in the vicinity of E_b. The formal aspects of the theory are similar to those used for the study of the resonant electron-phonon interaction for bound states.[7] Let us consider the Hamiltonian of a single electron moving in the crystal in the presence of an impurity and coupled with the lattice by the electron-phonon interaction H_1. We suppose that H_1 couples states $|\vec{k}, n_{q\mu}\rangle$ and $|b, n_{q\mu} + 1\rangle$, where in the first the electron is in a state with wave vector $\vec{k}$ in the conduction band and there are $n_{q\mu}$ phonons in mode $\vec{q}\mu$ present while in the second the electron is bound in the state b and there are $n_{q\mu} + 1$ phonons in the mode $\vec{q}\mu$. All other phonon modes remain unchanged. The matrix element of H_1 between these states will be designated by

$$\langle b, n_{q\mu} + 1 | H_1 | \vec{k}, n_{q\mu} \rangle = \beta_{q\mu} (n_{q\mu} + 1)^{1/2}. \tag{1}$$

The energy eigenvalues of the system are the real parts of the solutions of the equation

$$W = \epsilon_k + \sum_{q\mu} \frac{|\beta_{q\mu}|^2 (n_{q\mu} + 1)}{W + E_b - \hbar\omega_{q\mu} + \frac{1}{2} i\Gamma}. \tag{2}$$

Here, $\hbar/\Gamma$ is the lifetime of the state $|b\rangle$. The level corresponding to the electron in the conduction band with wave vector $\vec{k}$ is obtained by expanding the right-hand side of Eq. (2) in powers of W, keeping only the first power, and solving for W. In Eq. (2) we take for $n_{q\mu}$ its thermal-equilibrium value. This expansion is valid in view of the fact that the linewidth Γ is certainly non-negligible since in the case of AgBr the relevant state is not the ground state of the impurity but one which we assume to have an energy nearly one-LO-phonon energy above the ground state.

As expected this mechanism leads to shifts in the band edge and the zero-temperature effective mass, and in addition it gives rise to a temperature dependence of the polaron mass of the form

$$m^*(T) = m^*(0) + \mu \exp(-E_b/kT). \tag{3}$$

For our purposes, the significant dependence in temperatures gives a result which is in agreement with the data. We do not give a numerical estimate of the constant μ because it would require a detailed model of the impurity and of the vibrational spectrum of the crystal. This analysis is reserved for a future publication.

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Vanishing of the Ferroelectric and Antiferroelectric States in KH_2PO_2-Type Crystals at High Pressure*

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The ferroelectric phase of KH_2PO_4 and the antiferroelectric phase of $NH_4H_2PO_4$ vanish at hydrostatic pressures >17 and 33 kbar, respectively. The results are qualitatively discussed in terms of the coupled proton-lattice model developed by Kobayashi and others, and they reemphasize the important role of the hydrogen bond in these crystals. We discuss possible important changes with increasing pressure in the character of the ferroelectric mode in KH_2PO_4.

The purpose of this Letter is to report and discuss the observation of the vanishing of the ordered ferroelectric (FE) state in KH_2PO_4 (KDP) and antiferroelectric (AFE) state in $NH_4H_2PO_4$ (ADP) at high pressures and low temperatures. The work is the first of its kind, and the results reveal important information concerning the nature of the phase transitions in these important hydrogen-bonded crystals. Before presenting the results and discussing their implication, a brief account of the background which motivated the work is useful.

At high temperatures KDP and ADP are isomorphous—tetragonal $I\bar{4}2d$—and are paraelectric (PE). The crystal structure consists of tetrahedral PO_4 groups connected by a network of O-H• • •O hydrogen bonds which lie very nearly in the basal planes. On cooling, KDP transforms to an orthorhombic (Fdd_2) FE phase at 123°K with spontaneous polarization along the *c* axis, whereas ADP transforms to an orthorhombic ($P2_12_12_1$) AFE phase at 148°K. One of the most intriguing features of the behavior of these crystals is the crucial role played by the protons in the transition. This is most evidenced by the ~80% (for KDP) and ~60% (for ADP) increases in transition temperatures observed on complete deuteration.

Very extensive experimental and theoretical work has been reported, particularly on KDP, and several models for the FE behavior of this crystal have been proposed.[1] Although many questions remain unsettled,[1] the picture that has emerged and the point of view taken here is that the onset of ferroelectricity in KDP is triggered by an order-disorder transition of the protons in the H bonds, and that the motion of the protons is strongly coupled to the displacements of the other ions (particularly along the *c* axis). In the PE phase each proton can occupy either of two equilibrium positions along the H bond (i.e., there is a double-minimum potential), but it is ordered on one of them in the FE phase. The ordering is such that in a single domain all protons order near "upper" or "lower" oxygens of the PO_4 groups, depending on the polarity. In the AFE phase of ADP the ordering is such that the protons occupy one "upper" and one "lower" corner of each PO_4 tetrahedron, and the resulting coupling to the lattice is modified so as to cause antiparallel ionic displacements and an AFE phase. It has been recognized that the shape of the potential along the H bond is strongly dependent on the length of the bond. Since the H bond is mechanically the weakest link in the crystal structure, the properties of these crystals can be expected to be strongly pressure dependent. This was largely the motivation of the earlier low-pressure work.[2-6]

The details of the proton-lattice coupling and transition in KDP are very complicated, and quantitative models are lacking. However, a