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Nonlinear Transport Phenomena in AgCl and AgBr at High Electric Field*

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The mobility of electrons in zone-refined and impurity-doped AgCl and AgBr crystals at high electric fields has been investigated over the temperature range from $T=4°\mathrm{K}$ to $77°\mathrm{K}$ in order to examine the energy-momentum relation and to clarify the scattering mechanisms of slow and fast electrons in ionic crystals. The highest-purity crystals were obtained from ingots zone-refined 300 times in halogen atmospheres. Several crystals containing known amounts of iron impurity were also investigated. A fast-pulse technique was used to observe both the transient photoconductivity and the Hall mobility of the photoelectrons. The electrode geometry of Redfield was used in the Hall-mobility measurements. At high electric fields, the photocurrent $Q(T,E)$ was found to be proportional to the square root of the electric field E in pure AgCl and AgBr crystals at low temperatures. The Hall mobility $\mu_H(T,E)$ of fast electrons in pure crystals at low temperatures was observed to be a decreasing function of the electric field, thus explaining the $Q(T,E)$ data. Such nonlinear behavior is weaker in the impurity-doped crystals and gradually disappears even in pure crystals as the temperature rises, for the same range of the electric fields. These results are discussed in terms of the hot-electron theory. An energy-dissipation mechanism similar to the scattering due to the acoustical mode of lattice vibrations is suggested as effective for fast electrons in ionic crystals.

I. INTRODUCTION

THE theory of the polaron, namely, the electron in solids associated with virtual phonon clouds, has been of profound interest for physicists not only in the development of semiconductor physics but also as a testing ground for a new method in quantum field theory. Although there exist several difficult questions about how to separate the self-energy and scattering effects, how to validate the use of the Boltzmann equation, etc., it is of strong interest to pursue the energy-momentum relation of a polaron and its interaction with various types of phonons.

Theoretical physicists naturally first attacked the ground state of the polaron, so that the theory of the polaron in ionic crystals usually applies to a "slow electron" in thermal equilibrium with the crystal lattice. The mobility of "slow electrons" in ionic crystals has been calculated on this basis by several investigators.[1–4] Considerable amounts of experimental data are available, especially relating to the drift and Hall mobilities of slow electrons or holes in the silver halides.[5,6] As the electron departs from thermal equilibrium by gaining energy from an electric field, however, it is expected that the "slow-electron" concept will begin to fail. In order partly to study the higher-energy states of the polaron and partly to examine the scattering mechanisms of both slow and fast electrons in ionic crystals, the mobility of electrons in silver chloride at high electric field has been investigated. A nonlinear transport phenomenon was previously found in pure AgCl crystals at low temperatures.[7] We describe and discuss here further results of a thorough investigation of the nonlinear transport phenomena in both AgCl and AgBr, under various experimental conditions.

The experimental arrangements and problems are presented in Sec. II. In Sec. III, the experimental results showing nonohmic photoconductivity and Hall mobility in pure and impurity-doped AgCl and AgBr crystals at various temperatures are given. Discussion of the data, including the application of the hot-electron approach, is given in Sec. IV.

II. EXPERIMENTAL METHODS

Several experimental difficulties exist in observing high-electric-field effects in certain types of crystals. A general consideration was given by Shockley[8] in connection with Ryder's experiment on hot electrons in germanium.[9] As a result of the progress recently made in crystal purification and pulse technique, the requirements for high-electric-field experiments in ionic crystals have become almost the same as those in semiconductors, except for the question of how to create the conduction electrons, as discussed later.

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† A part of the experiment was carried out at the Institute for Solid State Physics, University of Tokyo.

[1] H. Fröhlich, H. Pelzer, and S. Zienau, Phil. Mag. **41**, 221 (1950); D. C. Langreth and L. P. Kadanoff, Phys. Rev. **133**, A1070 (1964); G. D. Mahan, *ibid.* **142**, 366 (1966).

[2] F. E. Low and D. Pines, Phys. Rev. **98**, 414 (1955).

[3] T. D. Schultz, Phys. Rev. **116**, 526 (1959); Y. Osaka, Progr. Theoret. Phys. (Kyoto) **25**, 517 (1961); R. P. Feynman, R. W. Hellwarth, C. K. Iddings, and P. M. Platzman, Phys. Rev. **127**, 1004 (1962); L. P. Kadanoff, *ibid.* **130**, 1364 (1963).

[4] A recent review of mobility theories has been given by D. C. Langreth, Ph.D. thesis, University of Illinois, 1964 (unpublished).

[5] R. S. Van Heyningen, Phys. Rev. **128**, 2112 (1962); R. K. Ahrenkiel and R. S. Van Heyningen, *ibid.* **144**, 576 (1966).

[6] T. Masumi, R. K. Ahrenkiel, and F. C. Brown, Phys. Status Solidi **11**, 163 (1965); D. C. Burhnam, F. C. Brown, and R. S. Knox, Phys. Rev. **119**, 1560 (1960).

[7] T. Masumi, Phys. Rev. **129**, 2564 (1963).

[8] W. Shockley, Bell System Tech. J. **30**, 991 (1951).

[9] E. J. Ryder and W. Shockley, Phys. Rev. **81**, 139 (1951).

We must first prepare perfect and extremely high-purity crystals. Ultrahigh-purity silver halide crystals were carefully cut out of ingots zone-refined 300 times in a halogen atmosphere, shaped, etched, washed, and annealed. Such insulator crystals have a sufficiently high resistivity to sustain high electric fields and to allow the avoidance of heating of the specimen and internal carrier multiplication. The procedures followed during sample preparation were described in Sec. II of Ref. 6.

Since there are few electrons in the conduction band of pure AgCl in thermal equilibrium, especially at low temperatures, the conduction electrons have to be excited out of the valence band. Short light pulses (duration 0.5–1.0 μsec), synchronized with the electric-field pulses and with a prior illumination by red light, were used to excite photoelectrons of density of the order of 10^9 per cm^3, small enough to avoid heating of the specimen. The earlier red-light illumination depolarizes the crystal after each pulse excitation.

The conduction electrons should have as high a mobility as possible, so that they can acquire energy through the electric field at a higher rate (fewer collisions). It is a necessary condition for obtaining a higher "electron temperature." It was found, using Redfield's technique,[10] that the Hall mobility of slow electrons, μ_H, is greater than 10^4 cm^2/V sec below 40°K, in annealed samples cut out of zone-refined ingots.[6] As the crystals are sufficiently perfect and pure, no serious problem of electron multiplication exists even though the electrons have a suitably high mobility (and a correspondingly large drift velocity) at low temperatures.

We should also avoid the effect of positive holes, if any. In general, they can be created in, or injected into, the crystal, recombine with the electrons, and/or modulate the conductivity. However, positive holes are usually much less mobile than electrons in the silver halides. The ratio of hole to electron ranges is less than ten per cent, being usually 10^{-2}–10^{-3} over the present temperature region.[11,12] Holes thus contribute little, especially in AgCl at low temperatures.

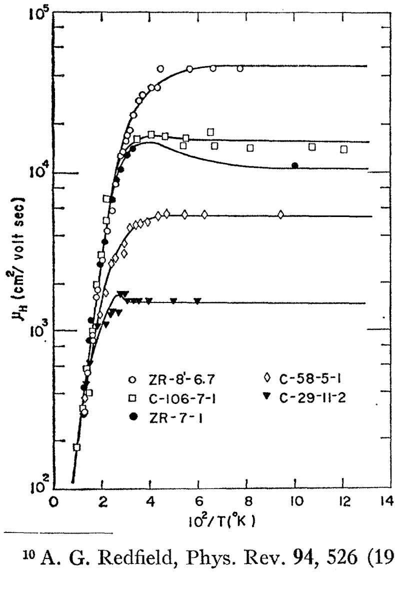

FIG. 1. Hall mobility of slow electrons at low electric field in pure and impurity-doped AgCl crystals as a function of temperature. Samples here were used also in Fig. 7.

TABLE I. Silver chloride crystals used in the measurements for Figs. 1 and 7 and their properties. Zone refining was performed in a Cl_2 atmosphere, while all the crystals except C-29-11-2 were annealed in a He atmosphere. The residual mobilities were measured in the temperature range 7 to 25°K.

Sample No.	Preparation	Residual mobility μ_H (cm^2/V sec)
ZR-8'−6.7	Zone-refined, U. I. (300 zones passed)	45 000
C-106-7-1	Zone refined, Kodak	17 000
ZR-7-1	Zone-refined, U. I. (100 zones passed)	12 000
C-58-5-1	Fe 6.0×10^{16} cm^{-3}	5 500
C-29-11-2	Fe 6.0×10^{17} cm^{-3} annealed in Cl_2 atmosphere	1 500

Finally, regardless of the high or low rate of gain of energy by the electrons, their heat dissipation inside the crystals should be minimized to stabilize the lattice temperature. A fast-pulse technique with Redfield's geometry[10] was adopted to overcome this difficulty. Methods used to measure the transient photoconductivity and the Hall mobility are almost the same as those in previous work,[6,7,13] with the addition of a few improvements in insulating the field-supplying wires and in using a quartz plate uniformly coated with NESA transparent semiconducting film with a resistance appropriate to the high electric field applied. The pulsed electric field (duration 500 μsec–1 msec) is applied singly or at a repetition rate of less than 1 pulse per sec. Since primary photoelectrons in the conduction band of the silver halides exist essentially during the light-pulse duration, the power delivered to the specimen during a cycle is completely negligible, although the electric-field pulse has a long duration. A low repetition rate guarantees that no heating of the crystal occurs. Special difficulties associated with the buildup of space charge and with the low signal-to-noise characteristic of high impedance material are also removed by Redfield's technique. In the Hall-mobility measurements, the magnetic field was kept sufficiently low so that the nonlinear effect at high magnetic fields[6] may be minimized.

Accordingly, most of the experimental difficulties associated with the high-electric-field effect in silver halides have been successfully removed.

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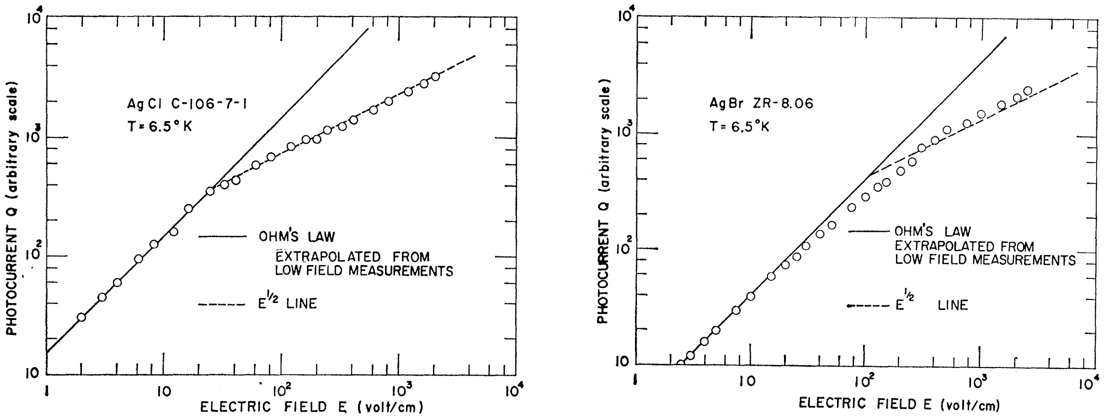
[10] A. G. Redfield, Phys. Rev. **94**, 526 (1954).

[11] R. S. Van Heyningen and F. C. Brown, Phys. Rev. **111**, 462 (1958).

[12] D. C. Burhnam, Ph.D thesis, University of Illinois, 1959 (unpublished). Unit range of an electron in AgCl at 80°K is usually of the order of 10^{-5}–10^{-6} cm^2/V. See Tables I and II of Ref. 11. Positive holes in AgBr are mobile to a small extent, but their range is in general much smaller than that of electrons under experimental conditions.

[13] F. C. Brown, J. Phys. Chem. Solids **4**, 206 (1958).



(a) (b)

FIG. 2. Typical examples of pulse height versus electric field for silver halides at $T=6.5$°K. The observed pulse height is proportional to the transient photocurrent Q. (a) AgCl; (b) AgBr.

An essential difference between the experimental requirements for the study of high-electric-field effects in most semiconductors and in insulators is that one has to excite the conduction electrons out of the valence band in ionic crystals in order to observe the primary photocurrent, whereas, in semiconductors, there is a finite number of electrons present in the conduction band in thermal equilibrium even at low temperatures. In both cases, however, in the pulse-height measurements of the current we observe a quantity proportional to the drift mobility of the electrons μ_d while keeping other quantities unchanged as the electric field increases. This will be discussed in Sec. III. Details of the zone-refining technique and the results of analysis,[6,14] the preparation of specimens,[6] the fast-pulse technique with Redfield's geometry[6,7,13] and the Hall-mobility data of slow electrons in silver halides[6] are available in the references cited.

III. EXPERIMENTAL RESULTS

The Hall mobility of slow electrons in pure and impurity-doped AgCl and pure AgBr crystals was studied as a function of temperature T.[6] Shown in Fig. 1, together with additional data, is the mobility of slow electrons $\mu_H(T,0)$ in pure and impurity-doped AgCl crystals measured in the present experiments. The impurity concentrations and crystal preparation used are listed in Table I, along with the values of residual mobility.

The high-electric-field effect in AgCl crystals of several grades of purity and in pure AgBr crystals has been investigated over the temperature range corresponding to the curves in Fig. 1. Typical examples of experimental results at $T=6.5$°K for ultrahigh-purity AgCl and AgBr crystals zone refined in a halogen atmosphere are shown in Fig. 2. Here the observed pulse heights of primary photocurrent Q (proportional to the induced charge per pulse) are plotted as a function of applied electric field E. Since the Schubweg of electrons, $w=\mu_d E\tau_t$, is short (negligible saturation or collection effect) over this temperature range, and the positive holes are less mobile than electrons in silver halides,[11,12] Q may be written in the form

$$Q(T,E)=ne\mu_d(T,E)E\tau_t(T,E)/D, \quad (1)$$

where n is the number of electrons released by a light pulse in the volume of crystal; e, the electronic charge; $\mu_d(T,E)$, the drift mobility of electrons; E, the electric field; $\tau_t(T,E)$, the average lifetime of an electron before trapping; and D the thickness of the crystal.

At low temperatures (below 34°K) and with a constant number of photons per pulse, it has been observed that Ohm's law, assuming $\mu_d(T,E)$ and $\tau_t(T,E)$ are independent of E, is valid only up to 20–30 V/cm. The departure from linearity in Fig. 2 was considered to be mainly due to a decrease in mobility, since Fig. 3 indicates that the relative ratio of Hall mobility $\mu_H(E)$ at

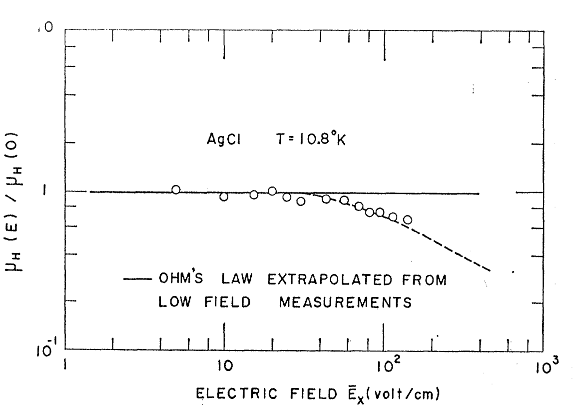


FIG. 3. Relative ratio of Hall mobility of electrons $\mu_H(T,E)$ at the electric field E to the low-field Hall mobility $\mu_H(T,0)$ in a pure AgCl crystal at $T=10.8$°K as a function of the effective electric field.

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[14] F. Moser, D. C. Burhnam, and H. H. Tippins, J. Appl. Phys. 32, 48 (1961).

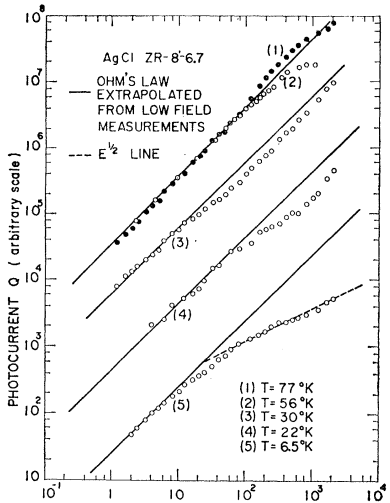

FIG. 4. Temperature variation of nonlinear photoconductivity of a pure AgCl crystal. (1) $T=77$°K; (2) $T=56$°K; (3) $T=34$°K; (4) $T=22$°K; (5) $T=6.5$°K. Relative values of photocurrent Q at fixed electric field less than E_c at various temperatures form the curve in Fig. 5.

electric field E to the low-field Hall mobility $\mu_H(0)$ at $T=10.8$°K is also a decreasing function of electric field. In Fig. 3, the electric field is the average component $\bar{E}_x$ as defined in Ref. 10. The difference between E and $\bar{E}_x$ and the difference in temperature between the data plotted in Figs. 2 and 3 are not serious, as noted in a previous paper,[7] and as also shall be inferred later from the data in Figs. 4 and 6. The Hall mobility $\mu_H(T,E)$ is related to the drift mobility $\mu_d(T,E)$ through a numerical factor of the order of unity, which is determined by the scattering mechanism of electrons and thus depends on temperature and electric field. If we ignore these minor corrections, the nonlinear behavior in Figs. 2 and 3 may be expressed as

$$\begin{aligned} Q&=\sigma E, & \mu&=a, & &\text{for } E\lesssim E_c,\\ Q&=\sigma' E^{1/2}, & \mu&=a'E^{-1/2}, & &\text{for } E\gtrsim E_c, \end{aligned} \tag{2}$$

and is found in both AgCl and AgBr at low temperatures. Here σ, σ', a, and a' are constants, and E_c is a critical electric field.

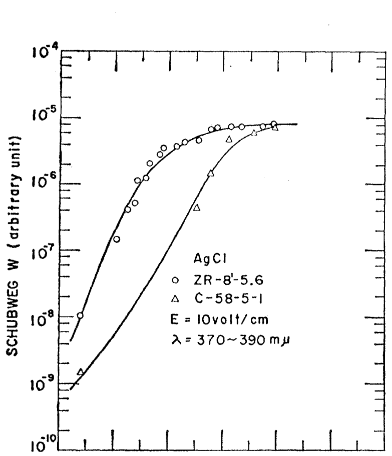

FIG. 5. Temperature dependence of Schubweg w of photoelectrons in pure and impurity-doped AgCl crystals at $E=10$ V/cm. Relative values of w for two crystals were normalized at $T=77$°K. (See Table I of Ref. 11.)

Further detailed investigations of the nonlinear photoconductivity in AgCl were performed. First, in ultrahigh-purity crystals at low temperatures, the validity of Eqs. (2) has been examined under various experimental conditions. The intensity of the illuminating light pulse was changed. On the order of 10^7–10^9 per cm^3 photoelectrons were released in a pulse, whose repetition rate was less than one per sec. The wavelength of the light pulse was usually set near the indirect transition region[15] where the absorption constant α is small, in order to produce a uniform electron distribution inside the crystal. Illumination was extended also to shorter wavelengths (350 mμ) where α reaches about 10^3 cm^{-1}, to see whether or not any surface effects are involved. Annealing processes caused no change in the photoconductivity as far as the electric field dependence is concerned, except in the case of impurity-doped crystals annealed in a halogen atmosphere. Space-charge effects were checked by changing the depolarizing ambient red light, and saturation effects were studied by using specimens having different thicknesses. It was confirmed that Eqs. (2) are valid, independent of the concentration of carriers, and no surface, strain, space-charge, and saturation effects are involved.

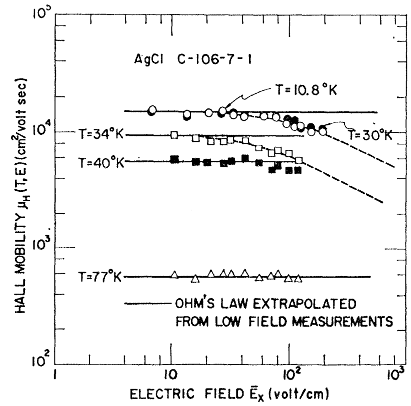

FIG. 6. Hall mobility $\mu_H(T,E)$ of electrons in a pure AgCl crystal at various temperatures as a function of the effective electric field.

Secondly, the nonlinear photoconductivity in a pure AgCl crystal at various temperatures was investigated with the results shown in Fig. 4. Here, the magnitude of photocurrent Q at a fixed electric field below E_c reflects the temperature dependence of the Schubweg, $w=\mu_d E\tau_t$. The nonlinear effect can be observed in its clearest form at low temperatures (below $T=12$°K) and remains even in the intermediate temperature region (between 12°K and 34°K), where poor stability of

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[15] F. C. Brown, T. Masumi, and H. H. Tippins, J. Phys. Chem. Solids 22, 161 (1961).

the temperature during the measurements results in some ambiguities. However, it gradually recedes as the temperature rises above 34°K. This fact also shows that no saturation effect is involved at low temperatures. The temperature dependence of the Schubweg is plotted in Fig. 5. At 77°K, impure crystals show a field dependence similar to that for pure crystals, and departures from linearity at high electric fields were found neither in the pure nor in the impurity-doped crystals, for the range of fields studied.

Thirdly, subsidiary measurements of the Hall mobility $\mu_H(T,E)$ as a function of E for a pure crystal were also carried out over a wider temperature region (up to 77°K) as shown in Fig. 6. The decrease in $\mu_H(T,E)$ at high electric field below $T=34$°K, together with the various temperature dependences of $\mu_H(T,0)$ in Fig. 1 indicates that the nonlinear effects, as in Fig. 4, appear in the temperature region where $\mu_H(T,0)$ is sufficiently high. It also suggests that the temperature difference between Figs. 2 and 3 is not serious. Hall-mobility data also guarantee that the effect is essentially free from trapping effects.

Finally, the effects of impurities on the nonlinear photoconductivity have been seen clearly at low temperatures (below $T=12$°K); Fig. 7 indicates the effect of iron impurities on the nonlinear photocurrent in AgCl crystals at $T=6.5$°K. The drift velocity of the electrons in each of the crystals was calculated from the low-field Hall-mobility data given in Fig. 1 by assuming that charged impurity scattering is dominant below E_c. In the case of impure crystals at low temperatures, the high-electric-field effect was observed to set in at a much higher value of electric field. Impurity scattering not only reduces the mobility of slow electrons at low temperatures but also smears out the nonlinear effect. Besides, depending on the impurity concentration and annealing processes, the various crystals have electron lifetimes varying over the rather wide range of at least an order of magnitude. Irrespective of these different trapping times, the nonlinear effect always appears to set in when the drift velocity of an electron attains about the velocity of the longitudinal acoustic wave c_s ($c_s=3.29\times10^5$ cm/sec for AgCl).

Magnetoresistance measurements in silver halides[16] also show the decrease of mobility as the electric field increases.

Consequently, it is reasonable to infer that such nonlinear transport phenomena are related to the change of intrinsic mobility of the electrons in pure AgCl and AgBr crystals at low temperatures.

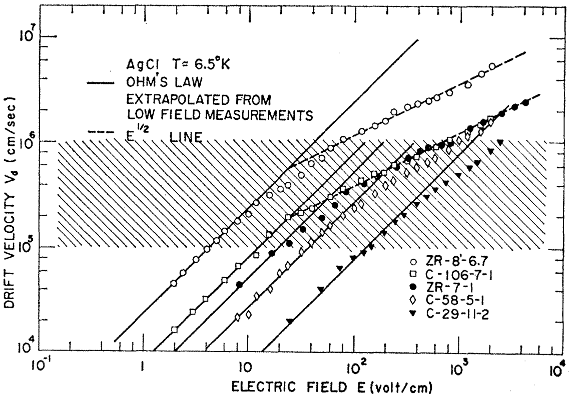

FIG. 7. Impurity effect of ferrous or ferric ion on the nonlinear photoconductivity of AgCl crystals at $T=6.5$°K. Drift velocity v_d for various crystals was calculated using the data in Fig. 1. Hatched zone indicates the region where v_d becomes of the order of the sound velocity c_s.

IV. DISCUSSION

The temperature dependence of the Hall mobility of slow electrons in AgCl crystals at low electric fields shown in Fig. 1 indicated that (1) the optical phonon scattering dominates at high temperature (above $T=34$°K), (2) the mobility of slow electrons at low temperatures is apparently dependent on sample purity, and (3) the scattering due to the acoustical mode of lattice vibrations becomes of considerable importance in high-purity crystals in an intermediate temperature range (between $T=34$°K and $T=12$°K) even for slow electrons.[6] A trial analysis of this situation is given in Fig. 8, where the Debye temperature calculated by the

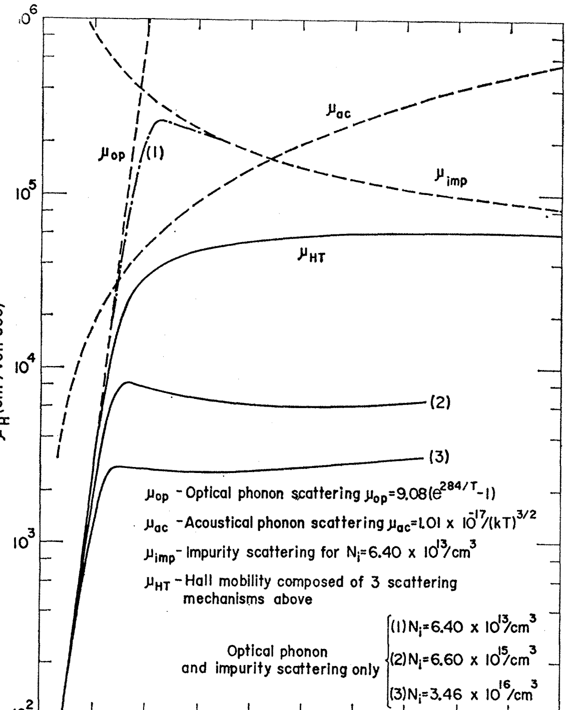

FIG. 8. Calculated curves of Hall mobility of slow electrons in AgCl as a function of $1/T$ in proper combinations of optical, acoustical, and charged impurity scattering, following the procedure described in Ref. 6.

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[16] H. H. Tippins and F. C. Brown, Phys. Rev. **129**, 2554 (1963).

Lyddane-Sachs-Teller relation was used, although the observed value is somewhat lower than expected. A similar situation is believed to be likely also for AgBr. In the case of AgBr, the acoustic phonon scattering was studied through the magnetic-field dependence of the pulse-height signal.[6]

Nonlinear transport phenomena in AgCl and in AgBr reported here occur when the electric field is enhanced while keeping the magnetic field sufficiently low. The low-electric-field Hall mobility of slow electrons $\mu_H(T,0)$ shown in Figs. 1 and 8 is ruled mainly by the residual density of charged impurity atoms even in zone-refined crystals at low temperatures, where the nonlinear electric-field effect can be seen in a distinct form. However, Fig. 7 indicates that there is little smearing effect due to impurities in the nonlinear photoconductivity of zone-refined crystals. Besides, the scattering by charged impurity centers is likely to be less important for the scattering of fast electrons,[17] since the fast electrons have a smaller cross section than the slow electrons in Rutherford scattering.

Matz and Garcia-Moliner[18] suggested the importance of dipole scattering in determining the residual mobility. In silver halides, divalent or trivalent cation impurity atoms form dipoles with compensating vacancies. Lowering the temperature freezes these dipoles which scatter electrons. This problem was discussed in previous paper.[6,18] The dipole scattering probability p_d, however, has an energy dependence ($p_d \propto \epsilon^{-1/2}$) weaker than, but of a type similar to, that of charged impurity scattering ($p_i \propto \epsilon^{-3/2}$) for fast electrons. Furthermore, the scattering by static imperfections is primarily elastic and cannot provide the energy transfer mechanism for fast electrons in a high electric field. Some type of inelastic scattering, such as that due to lattice vibrations, becomes increasingly important at high fields.

First, as the most effective among the mechanisms of inelastic scattering, we may consider the scattering by the optical mode of lattice vibrations. Silver halides have a coupling constant of the order of 2, for which the intermediate coupling theory is suitable. However, as seen in Figs. 1 and 8, the temperatures below 34°K freeze the optical phonons, so that absorption of optical phonons by electrons is rare. On the other hand, in most of the electric field range, the drift velocity of electrons in Fig. 7 corresponds to values of average energy much smaller than the optical phonon energy ($\theta = 225$–$284°$K). This means that optical phonon emission by electrons also cannot occur. Therefore, the optical phonons are likely to play a small role in the nonlinear effect at low temperatures.

At low fields, Figs. 2 and 4 show that Ohm's law is valid up to the critical field E_c. The small values of $E_c = 10$–30 V/cm for pure crystals suggest that the amounts of energy loss per collision involved are rather small. At high fields, the observed dependence on $E^{1/2}$ also suggests that a scattering mechanism whose scattering probability increases in proportion to the electron speed v_1 becomes important if the energy lost per collision for fast electrons is assumed proportional to v_1^2. Accordingly, the inelastic scattering mechanism looked for might involve the acoustical mode of lattice vibrations.[7,8]

As previously reported[6] and shown in Fig. 1, the Hall mobility of a slow electron in high-purity AgCl crystals below $T = 34°$K (in AgBr below $T = 27°$K) down to 4°K is quite high [e.g., $\mu_H(T,0) \simeq 2$–4.5×10^4 cm^2/V sec in zone-refined AgCl crystals], whereas the velocity of the longitudinal acoustic wave c_s is rather small in ionic crystals ($c_s = 3.29 \times 10^5$ cm/sec for AgCl, 2.96×10^5 cm/sec for AgBr).[19] Also, it was deduced from the magnetoresistance measurements[16] that the lowest conduction bands in AgCl and AgBr are of standard form, namely, s-like with a minimum at $\mathbf{k} = 0$, and thus states belonging to the Γ_1 representation.[20] Hence, no mechanism like intervalley scattering should be involved. Consequently, we expect hot-electron phenomena to set in at fairly low electric fields.

Actually, estimates of the critical drift velocity v_{dc} for departure from Ohm's law give values comparable with the sound velocity c_s. Rather low experimental values of v_{dc} indicate an energy dissipation mechanism in which the average energy lost per collision is quite small, such as is the case of acoustical phonons. The similarity between the two curves of $\mu_H(T,E)$ for $T = 10.8°$K and 30°K in Fig. 6 also suggests that the scattering is mainly due to acoustic phonon emission rather than absorption. Unlike the case for nonpolar semiconductors, the interaction between a polaron and acoustic phonons in ionic crystals may be of the polar type described by Meijer and Polder[21] rather than of the usual deformation potential type discussed by Bardeen and Shockley.[22] This may be the case if the polar acoustic scattering has the stronger coupling constant. There is, however, no way to distinguish these types of scattering for polarons since they have the same energy and temperature dependences. In any case, it is clear that the acoustic phonon interaction is important in the nonlinear transport phenomena in silver halides.

A few questions, however, still remain. First, around E_c, the scattering of polarons by static imperfections provides quite an enigma. We have shown in Fig. 1 that the residual mobility of slow electrons at low temperatures is structure-dependent, whether determined by the charged impurities or atomic dipoles. By weigh-

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[17] E. M. Conwell, Phys. Rev. **90**, 769 (1953).

[18] D. Matz and F. Garcia-Moliner, J. Phys. Chem. Solids **26**, 551 (1965).

[19] D. L. Arenberg, J. Appl. Phys. **21**, 941 (1950); D. S. Tannhauser, L. J. Bruner, and A. W. Lawson, Phys. Rev. **102**, 1276 (1956).

[20] F. Bassani, R. S. Knox, and W. B. Fowler, Phys. Rev. **137**, A1217 (1965).

[21] H. J. G. Meijer and D. Polder, Physica **19**, 255 (1953).

[22] J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

ing the probable magnitude of impurity (or dipole) scattering and acoustic phonon scattering at low fields, it is possible to anticipate the occurrence of high-field effects where the acoustic phonon scattering should become dominant because of its stronger energy dependence in comparison with that of impurity (or dipole) scattering. An actual estimate leads us to the conclusion that the impurity (or dipole) scattering is rather strong at low fields, so that the critical field should be much higher than the observed E_c. In the high-field experiments, however, the static imperfections behave as rather weaker scattering centers of fast electrons than of slow electrons for some yet unknown reason.

Second, the usual high-temperature approximation in calculating the collision integral may not be adequate. The lattice temperatures at which the nonlinear effects appear are rather low. The highest-energy acoustic phonons involved in scattering correspond to an energy of the order of $2c_s m_p^* v_1 = (4c_s/v_1)k_B T_p$,[8] which is large for fast electrons. Here, m_p^* is the effective mass of polarons; k_B, Boltzmann's constant; T_p, the polaron temperature.[23] The classical equipartion law of energy among the acoustical phonons then breaks down,[24] and the collision integral becomes fairly complicated. The simple $E^{1/2}$ dependence observed in pure crystals at low temperatures under high-electric fields is thus a surprise. Also strange is the fact that the $E^{1/2}$ law in silver halides is valid over regions of E rather wider than in germanium and silicon.

Third, at the highest fields, since fast polarons should have a rather high energy, it should be possible for them to emit optical phonons even at low temperatures. Optical phonon emission should result in current saturation at high electric fields, but this was not observed.

Finally, the "slow-electron" concept in the polaron theory will begin to fail at high fields, where the polaron has an energy sufficiently above the ground-state energy. A few theoretical studies of the energy-momentum relation of these fast polarons have been developed.[25,26] The polaron mass is expected to vary with its energy, although little experimental knowledge has been accumulated so far. The questions brought up here have not yet been solved and require further studies, both theoretical and experimental.

Although there is as yet no complete explanation of the nonlinear transport phenomena observed in silver halides, the clearly observed $E^{1/2}$ dependence suggests the importance of the acoustical modes of lattice vibrations when a polaron in pure AgCl or AgBr crystals at low temperatures moves around in high electric fields. Similar nonlinear phenomena have been found in KCl,[27] KBr,[28] and TlCl.[29] These facts indicate that the phenomena are intrinsic to ionic crystals. Since the number of electrons produced by illumination is rather small in practice, no phonon buildup effect like that seen in piezoelectric semiconductors[30–32] should be involved. The nonlinear transport phenomena in AgCl and AgBr may be due to Čerenkov-like emission of the acoustical phonons by a single polaron. Anharmonic interaction among the acoustical and optical phonons may convert them into each other. The possibility of microwave emission by electrons accelerated through dielectric materials was discussed by Lashinsky.[33] The importance of the acoustical mode of lattice vibrations for the scattering of high-energy electrons in ionic crystals was noted several years ago by Seitz.[34]

V. CONCLUSION

Polaron nonlinear transport phenomena at high-electric fields are observed in zone-refined AgCl crystals below $T=34°\mathrm{K}$, and in zone-refined AgBr crystals below $T=27°\mathrm{K}$. At high-electric fields, it is clearly observed that the photocurrent $Q(T,E)$ is proportional to the square root of electric field in pure crystals at low temperatures. Experimental results obtained by measurements of the Hall-mobility $\mu_H(T,E)$ show that the mobility of fast electrons in pure crystals at low temperatures is a decreasing function of electric field, in correspondence with the photoconductivity data. The Hall-mobility measurements also guarantee that the nonlinear phenomena are free from trapping effects. Such high-electric-field effects are weaker in impurity-doped crystals and gradually disappear even in pure crystals as the temperature rises, for the same range of electric fields. An energy dissipation mechanism similar to the scattering due to the acoustical mode of lattice vibrations is suggested for these fast polarons. It is conceivable that a higher-energy conduction electron, a fast polaron, interacts mainly with the acoustical mode of lattice vibrations in ionic crystals. Čerenkov-like emission of the acoustic phonons by a single polaron may underline the phenomena.

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Self-Consistent Pair Correlations in Mott-Type Insulators

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A simple cubic hydrogenic lattice with the Hubbard Hamiltonian is used as a model for Mott-type insulators. A new self-consistent approximation is developed by the decoupling of four-particle Green's functions, leading to a higher-order Hartree-like eigenvalue equation for electron-hole Green's functions. This equation is an improvement over the previously used Ω approximation. The solution of the eigenvalue equation leads to the conjecture that an exact solution (i.e., one without decoupling) would result in each atom having exactly one electron.

I. INTRODUCTION

The properties of most insulators can be explained by conventional energy-band theory. There are some exceptions to this rule. In this paper another model will be investigated.

Mott[1] has called attention to the fact that metal atoms at large separations should constitute an insulator. A model of these Mott-type insulators has been investigated by Hubbard[2] and by Kemeny.[3–5] Both authors used Zubarev[6] two-time Green's functions. Hubbard employed the one-electron, and Kemeny the two-particle electron-hole variety. The latter approach shows that under appropriate circumstances bound electron-hole pairs appear, which is the original picture of Mott.

In I we defined the retarded electron-hole Green's function of the Zubarev type.

$$G_{ijj'i'}(t-t')=\langle\langle c_{i\sigma}^{\dagger}(t)c_{j\sigma}(t);c_{j'\sigma}^{\dagger}(t')c_{i'\sigma}(t')\rangle\rangle. \tag{1.1}$$

The equation of motion for this Green's function contained a higher-order correlation term

$$J\langle\langle(n_{j-\sigma}-n_{i-\sigma})c_{i\sigma}^{\dagger}c_{j\sigma};c_{j'\sigma}^{\dagger}c_{i'\sigma}\rangle\rangle. \tag{1.2}$$

We incorporated $\langle(n_{j-\sigma}-n_{i-\sigma})\rangle$ into an effective potential, still denoted by J, without giving a prescription as to how it should be calculated. Thus the calculation was not self-consistent.

The primary purpose of this paper is the derivation and solution of a self-consistent equation valid in the insulating range. This will be done using the Martin-Schwinger[7] many-time Green's-function technique. In the insulating range, all electron-hole pairs are bound. Such a situation can be treated by considering two-particle electron-hole Green's functions. It is not even necessary to solve for the entire electron-hole Green's function; it is enough to obtain its homogeneous part. This is obvious from I, where we found that bound states were characterized by the homogeneous part of the equation for the spectral representation.

II. TRANSFORMATION OF THE HAMILTONIAN

In I we used the Hubbard Hamiltonian[2]

$$H=\sum_{ij}\sum_{\sigma}T_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}+J\sum_{i}n_{i\sigma}n_{i-\sigma}. \tag{2.1}$$

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