Cyclotron Resonance of Polarons in the Silver Halides: AgBr and AgCl

J. W. Hodby and G. P. Russell
Clarendon Laboratory, University of Oxford, Oxford OX1 3PU, United Kingdom

F. M. Peeters and J. T. Devreese[a]
Departement Natuurkunde, University of Antwerp, B-2610 Wilrijk, Belgium

and

D. M. Larsen
Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 7 June 1985; revised manuscript received 24 December 1986)

A quantitative test of the theory of large polarons has been achieved by precise measurement of the cyclotron resonance of polarons in silver halides in magnetic fields up to 16 T. We find that a good agreement between the measurements and their theoretical interpretation is achieved by variational polaron theory, but the best quantitative agreement is achieved by a recent theory of the magnetoabsorption of polarons, based on a generalization of the Feynman polaron model.

PACS numbers: 71.38.+i, 76.40.+b

Few experiments exist to provide a quantitative test of the validity of currently accepted polaron theories. The pioneering studies of high-frequency cyclotron resonance in III-V and II-VI semiconductors[1-3] showed the power of an experiment in which large polarons are probed spectroscopically at a frequency approaching that of the longitudinal optical phonon. The polaron effects manifest themselves in two ways: first, as a discontinuity in the measured cyclotron frequency as the applied magnetic field is varied to sweep the cyclotron frequency through that of the longitudinal optical phonon and, second, as a frequency-dependent or nonparabolic carrier "mass" at cyclotron frequencies below that of longitudinal optical phonon. The limitation to such experiments in III-V and II-VI semiconductors is set by the precision to which the available magnetic field can be determined and by the small magnitude of the effects to be measured, comparable with the nonparabolicity of the band states themselves.

More suitable candidates for a detailed comparison between theory and experiment exist within the alkali and silver halides. Here the wide band gap ensures that the rigid-band states exhibit little deviation from a parabolic dependence of energy on wave vector, while the highly ionic lattice produces polar coupling constants in the range from 1 to 5. Electron polaron masses in low magnetic field range from $\sim 0.3 m_e$ in AgBr to $\sim 1.0 m_e$ in RbCl,[4] where m_e is the mass of the free electron. These large band masses make it impracticable with present steady magnetic fields to make the cyclotron frequency exceed the frequency of the longitudinal optical phonon. Measurements must therefore concentrate on precise measurement of cyclotron resonance at lower magnetic fields. Early measurements in AgBr with use of magnetic fields up to 10 T in conjunction with a cyanide laser were reported in 1974.[5] We now describe measurements of the cyclotron resonance of electrons in AgBr and in AgCl with use of the magnetic fields up to 16 T available in the 5-cm-bore hybrid magnet at the University of Oxford. The silver halides are photoconducting insulators with indirect band gaps of about 3 eV and with electron mobilities exceeding 140000 $cm^2 V^{-1} s^{-1}$ at 4 K. Carriers are excited across the indirect gap by short pulses of light from a suitably filtered xenon flash lamp. The specimen is placed between plane parallel electrodes and cooled by direct immersion in liquid helium. The polarity of the electric field between the electrodes is reversed between successive flashes of light to prevent buildup of space charge within the specimen. The movement of the electrons before they are retrapped induces pulsed photocharges on the electrodes. The excitation of carriers between Landau levels in cyclotron resonance results in changes in their scattering rates. The resulting changes in the measured photocharges are averaged and recorded as the applied magnetic field is swept. Cyclotron resonance is stimulated by a backward-wave oscillator at 137 GHz, and at higher frequencies by a pulsed far-infrared laser using methanol vapor, optically pumped by a 3-J transverse-excitation atmospheric CO_2 laser. The magnetic field is measured by search coil and integrating voltmeter interpolating between NMR calibration points achieved with proton and cesium resonances. The laser wavelengths are measured by a Fourier-transform spectrometer operated as a Michelson interferometer.

Typical measurements of differential photocurrent cyclotron-resonance signal in AgBr taken at a lattice temperature of 4.2 K and with use of low far-infrared power are shown in Fig. 1. The observed transitions represent the excitation of conduction electrons between

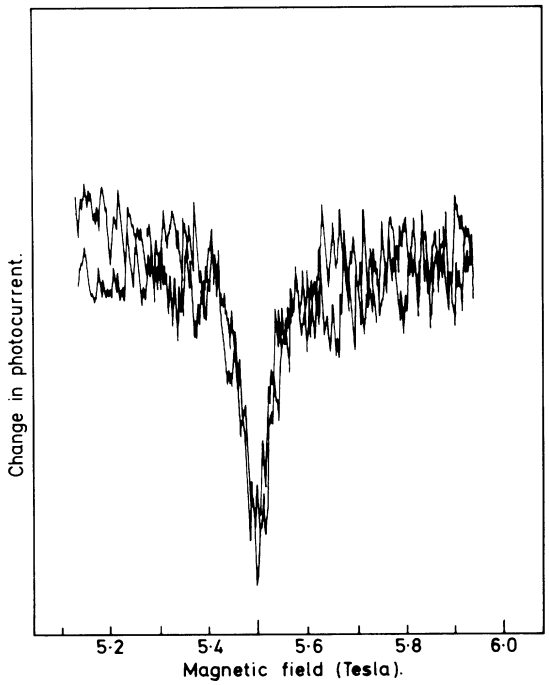

FIG. 1. Far-infrared cyclotron resonance of electrons in AgBr at 4.2 K. Laser frequency is 525 GHz.

the first and second Landau levels in the applied magnetic field. At higher far-infrared powers the resonance is broadened, and imperfectly resolved structure appears on the high-magnetic-field side of the resonance within the broadened line width. We believe that we are then seeing the effects of sequential excitation up the ladder of broadened Landau levels. These observations will be described in detail at a later time. In specimens of poorer quality the carrier mobility is smaller, giving a broader resonance. Of more serious consequence within the present studies, the lifetime of an electron before trapping is smaller in an impure specimen; the electrons do not have time to cool to equilibrium with the lattice and the resonance is broadened asymmetrically by the distribution in mass associated with their motion parallel to the magnetic field. Similar observations were made in AgCl.

The primary parameters to enter polaron theory are the rigid-lattice band mass m_b, the frequency of the longitudinal optic phonons at the zone center ω_{LO}, and the polaron coupling constant α. We choose to use only one free parameter, the band mass m_b, for which the present measurements provide the best data presently available. We take the phonon energy and the static and optical dielectric constants ε_0 and ε_∞ given in Table I. The polaron coupling constant is then given by

$$\alpha=\frac{e^2}{2}\left(\frac{2m_b\omega_{LO}}{\hbar}\right)^{1/2}\frac{1}{\hbar\omega_{LO}}\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_0}\right).$$

We find that α has the values 1.53 in AgBr and 1.84 in AgCl. The early calculations of polaron properties are not sufficiently accurate at such coupling strengths: (a) Rayleigh-Schrödinger perturbation theory[6] breaks down for $\alpha>1$ and is only valid for small magnetic fields, i.e., for $\omega_c/\omega_{LO}\ll 1$ where ω_c, the cyclotron frequency for a rigid-lattice band mass, is given by eB/m_b. (b) Wigner-Brillouin perturbation theory (WBPT)[7] is not exact to order α for ω_c/ω_{LO} near to 1. (c) Improvements to WBPT (IWBPT)[7,8] are argued to be correct to order α and valid for magnetic fields up to at least $\omega_c/\omega_{LO}\sim 1$. IWBPT was successfully applied to the study of InSb[7] and GaAs.[8] It is, however, inappropriate when α is comparable to, or greater than, unity.

For AgBr and AgCl, a theory is needed which goes beyond perturbation theory. Until recently the theory with the largest range of validity in α while allowing for a magnetic field was the variational theory of Larsen[9] which was successfully applied[3] to CdTe for ω_c/ω_{LO} in the range 0–0.6 and which was used for the interpretation of the earlier experiments on AgBr.[10]

An alternative theory appropriate for large α and large magnetic field is a recent generalization of the Feynman-Hellwarth-Iddings-Platzman[11] theory of the polaron containing the axial symmetry required in the presence of a magnetic field.[12,13] Extending this approach, Peeters and Devreese[14] (PD) showed that the magneto-optical absorption spectrum of polarons at $T=0$, in the Faraday-active-mode configuration (in

TABLE I. Summary of physical parameters and the results of the theoretical fits where m_b is the fitted rigid-lattice band mass, m_p is the polaron mass in the limit of low temperature and of low magnetic field, and m_e is the mass of the free electron. The stated error limits represent only the experimental uncertainty (FWHM).

	ε_∞	ε_0	λ_{LO}^{-1} (cm^{-1})	α	m_b/m_e	m_p^*/m_e	Theory
AgBr	4.68	10.60	140	1.56	0.2185(3)	0.2837(4)	Larsen (parabolic band)
				1.54	0.2124(3)	0.2824(4)	PD (parabolic band)
				1.53	0.2108(3)	0.2818(4)	PD (nonparabolic band)
AgCl	3.97	9.50	196	1.88	0.2928(15)	0.4015(20)	Larsen (parabolic band)
				1.84	0.2809(15)	0.3994(20)	PD (parabolic band)
				1.84	0.2805(15)	0.3988(20)	PD (nonparabolic band)

which cyclotron resonance experiments are performed), can be written as

$$\lim_{\varepsilon \to 0} \mathrm{Re}\{1/[z-\omega_c-\Sigma(z)]\},$$

where $z=\omega+i\varepsilon$ and $\Sigma(z)$ is a memory function which takes account of all the polaron internal states, important at large α, and of all the Landau levels. The explicit result for $\Sigma(z)$ depends on the parameters of the anisotropic Feynman polaron model which are determined by a variational calculation of the polaron ground-state energy.[12] This theory reduces to the Feynman-Hellwarth-Iddings-Platzman theory when $\omega_c/\omega_{LO}=0$ and also to perturbation theory,[15] successfully applied to InSb,[16] when $\alpha \ll 1$. At zero temperature and when $\omega < \omega_{LO}$ we have $\mathrm{Im}\Sigma(\omega)=0$. The position of the cyclotron resonance line is then determined by the equation

$$\omega-\omega_c-\mathrm{Re}\Sigma(\omega)=0.$$

This equation has solutions $\omega=\omega_c^*$. A calculated polaron "mass" m_p^* follows from the relation $\omega_c^*=eB/m_p^*$. In the limit of zero magnetic field strength the mass reduces to that obtained by Feynman[17] which is thought to be an excellent approximation at all values of α.

For comparison with experiment it is necessary to estimate the nonparabolicity of the rigid-lattice conduction-band states. This was done by use of effective-mass theory with allowance only for the interactions between the conduction band and the highest valence bands. The estimated contribution from this source to the increase in cyclotron mass for transitions between the lowest two Landau levels at the highest magnetic field used here is only 0.41% in AgBr and 0.24% in AgCl, while the observed increase in mass is ~12% in AgBr and 9% in AgCl. Following Larsen,[9] it is then possible to apply polaron theory to a parabolic-band conduction electron and to use Kane theory to add the small band nonparabolicity. Given the small magnitude of this correction, and the unknown but small corrections of opposite sign from higher conduction bands, the theoretical calculations have been done both with and without such two-band corrections.

In Figs. 2 and 3 we show a comparison between our measurements in AgBr and AgCl, the variational theory of Larsen,[10] and the path-integral theory of PD.[14] For illustrative purposes we show the fit of the PD theory both for assumed parabolic rigid-band states and also when the small corrections of a two-band Kane model are added. In each case the band mass was adjusted to fit the experimental point at 525 GHz. The quantitative details of the fit are given in Table I where the values deduced for band mass and for coupling constant are shown. For comparison we mention the perturbation result (IWBPT) for AgBr at $B=15.3$ T which gives $m^*/m_e=0.0301$, which should be compared with the ex-

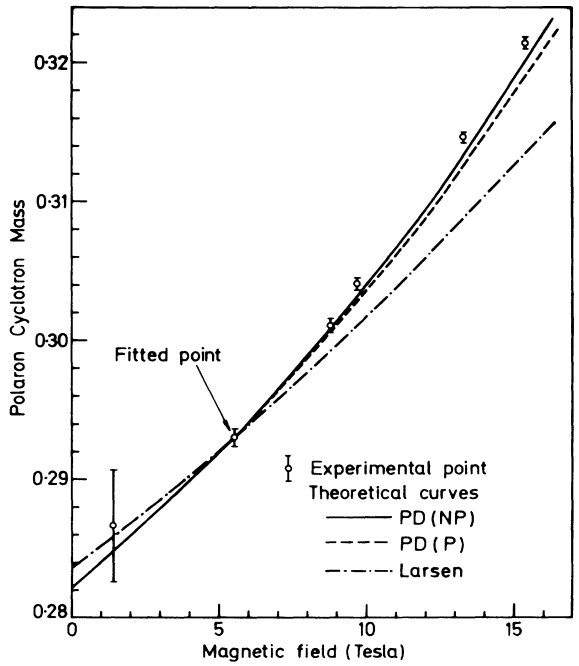

FIG. 2. Cyclotron resonance of electrons in AgBr: comparison of experiment and theory. PD (NP): Peeters and Devreese (Ref. 14) with two-band Kane corrections. PD (P): Peeters and Devreese (Ref. 14) with parabolic band. Larsen: Larsen (Ref. 10) with parabolic band.

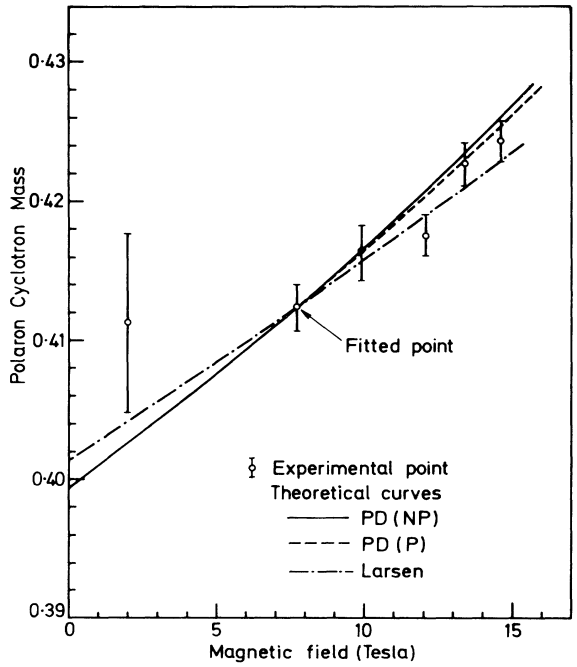

FIG. 3. Cyclotron resonance of electrons in AgCl: comparison of experiment and theory. PD (NP): Peeters and Devreese (Ref. 14) with two-band Kane corrections. PD (P): Peeters and Devreese (Ref. 14) with parabolic band. Larsen: Larsen (Ref. 10) with parabolic band.

perimental result 0.321.

The close agreement between experiment and theory is most encouraging given the fundamentally different theoretical approaches to the large polaron and the absence of free parameters in the theory (except the otherwise unknown band mass). It would appear, however, that the variational approach of Larsen currently underestimates the nonparabolicity of the polaron eigenstates. This supposition is confirmed by recent perturbation calculations of the cyclotron energy of the two-dimensional polaron.[18] Our results provide evidence that the Fröhlich Hamiltonian and the dielectric continuum model are able to treat quantitatively the polar interaction between carriers and lattice even in materials as ionic as the silver halides.

The specimens of specially purified AgBr and AgCl used in this investigation were supplied by Dr. F. Moser of the Eastman Kodak Company and by Professor T. Masumi of the University of Tokyo. One of the authors (F.M.P.) acknowledges financial support from the National Fund for Scientific Research, Belgium. This work was partially supported by Fonds voor Kollektief Fundamenteel Onderzoek (Belgium), Project No. 2.0072.80. The Francis Bitter National Magnet Laboratory is supported by the National Science Foundation through its Division of Materials Research.

---

[a]Also at University of Antwerp (Ryksuniversitair Centrum te Antwerpen), Antwerp, Belgium, and Technische Universiteit, Eindhoven, The Netherlands.

[1]D. H. Dickey, E. J. Johnson, and D. M. Larsen, Phys. Rev. Lett. **18**, 599 (1967).

[2]C. J. Summers, P. G. Harper, and S. D. Smith, Solid State Commun. **5**, 615 (1967).

[3]J. Waldman, D. M. Larsen, P. E. Tannenwald, C. C. Bradley, D. R. Cohn, and B. Lax, Phys. Rev. Lett. **23**, 1033 (1969).

[4]J. W. Hodby, J. Phys. C **4**, L8 (1971).

[5]J. W. Hodby, J. G. Crowder, and C. C. Bradley, J. Phys. C **7**, 3033 (1974).

[6]D. M. Larsen, Phys. Rev. **142**, 428 (1966).

[7]D. M. Larsen and E. J. Johnson, J. Phys. Soc. Jpn., Suppl. **21**, 443 (1966).

[8]G. Lindemann, R. Lassnig, W. Seidenbusch, and E. Gornik, Phys. Rev. B **28**, 4693 (1983).

[9]D. M. Larsen, in *Polarons in Ionic Crystals and Polar Semiconductors,* edited by J. T. Devreese (North-Holland, Amsterdam, 1972), p. 237.

[10]D. M. Larsen, J. Phys. C **7**, 2877 (1974).

[11]R. P. Feynman, R. W. Hellwarth, C. K. Iddings, and P. M. Platzman, Phys. Rev. **127**, 1004 (1962).

[12]F. M. Peeters and J. T. Devreese, Phys. Rev. B **25**, 7281 (1982).

[13]F. M. Peeters and J. T. Devreese, Phys. Rev. B **28**, 6051 (1983).

[14]F. M. Peeters and J. T. Devreese, Phys. Rev. B **34**, 7246 (1986).

[15]J. Van Royen, J. De Sitter, L. F. Lemmens, and J. T. Devreese, Physica (Amsterdam) **89B**, 101 (1977).

[16]J. Van Royen and J. T. Devreese, Solid State Commun. **40**, 947 (1981); J. Van Royen, J. De Sitter, and J. T. Devreese, Phys. Rev. B **30**, 7154 (1984).

[17]R. P. Feynman, Phys. Rev. **97**, 660 (1955).

[18]D. M. Larsen, to be published.