POLARON ZEEMAN EFFECT IN AgBr†

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We report observation and measurement of the Zeeman effect of a P state of a bound conduction electron in AgBr. The Zeeman mass which we observe is ~19% greater than the low-frequency cyclotron mass. This mass shift can be understood quantitatively as a new polaron self-energy effect.

Brandt and Brown have recently shown that by illuminating AgBr crystals at liquid-helium temperature with band-to-band light, absorption in the infrared can be induced.[1-3] The most striking feature of this induced absorption is a strong narrow line at 168 cm^{-1} which was interpreted by the above authors as the transition of a polaron bound in a Coulomb field from a $1S$ to a $2P$ state. Since the static dielectric constant[4] ($\epsilon_0 = 10.6$), the longitudinal optical-phonon frequency[5] ($\hbar\omega_{\text{LO}}$), and the cyclotron mass[6] ($m_c \simeq 0.27 m_e$) are known for AgBr at liquid-helium temperature, it is possible to test a simple hydrogenic theory for the energy levels of the bound electrons. The agreement between the calculated energy levels and the observed transition energy is reasonable considering the uncertainty of the nature of the positive-charge distribution.

We have studied the Zeeman splitting of the 168-cm^{-1} line in a dc magnetic field. Our results, consistent with the interpretation that the transition is S to P, determine a P-state Zeeman mass (m_Z) defined by $E_{P,+1} - E_{P,-1} = \hbar eH/m_Z c$, where $E_{P,M}$ is the energy of the observed P state with orbital angular momentum M in magnetic field H. In a parabolic band with no electron-phonon interaction, m_Z is simply equal to the cyclotron mass. AgBr, which has a parabolic conduction band, is quite polar; its conduction-band electron–LO phonon coupling strength is far from negligible[7] ($\alpha \approx 1.6$). As we shall show, this interaction increases m_Z from the low-frequency cyclotron-resonance mass. We here report observation and calculations of such a shift.

A single crystal of AgBr, clamped firmly to the cold finger of a helium Dewar, was placed between the pole pieces of a Varian magnet, at the image point of the exit slit of a vacuum infrared grating spectrophotometer. Band-to-band light, which was focused on the sample by a separate optical system, was provided by a 200-W high-pressure mercury lamp, filtered through a narrow-band dielectric filter. Infrared light from the mercury lamp was rejected by passing the band-to-band light through a thick (~2-cm) quartz filter. A black polyethylene filter at liquid-helium temperature was placed in front of the bolometer detector to prevent the bolometer from responding to any scattered band-to-band light. In the experimental arrangement, it was possible to make measurements with the infrared light polarized either perpendicular or parallel to the magnetic field, but only with the light propagating perpendicular to the magnetic field. The experimental procedure was to measure first the transmission I_0 of the crystal before band-to-band light was turned on and then the transmission I_s of the crystal with the band-to-band light on at various magnetic fields. The induced absorption coefficient $[\ln(I_0/I_s)]$ was calculated by a computer and plotted digitally versus wave number (Fig. 1).

As seen in Fig. 1, the 168-cm^{-1} line splits into three components, the center line having polarization $E \parallel H$ and the outer lines having polariza-

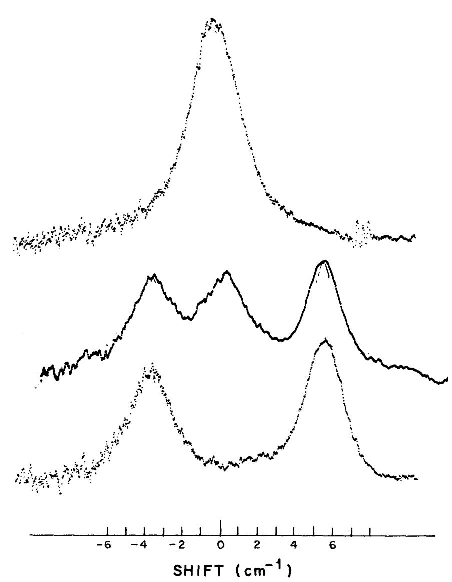

FIG. 1. Induced absorption of the "168-cm^{-1}" line. The top curve is a plot of the zero-field absorption coefficient. The middle and lower curves show the Zeeman split absorption at 32 kG as observed in unpolarized infrared radiation and in radiation polarized perpendicular to the applied field, respectively.

tion $E\perp H$. At low fields, overlap of the lines (due to instrumental resolution of 1.6 cm^{-1} and the natural linewidth) made a determination of the line positions unreliable. From 20 to 32 kG with $E\perp H$, where the lines were well separated and highly symmetric, it was possible to determine the position of the line centers with a precision of about ± 0.04 cm^{-1}. A plot of the line shifts ($E_\pm$) from the zero-field line center at 167.6 cm^{-1} versus magnetic field is given in Fig. 2. It is possible to fit these data with the equation $E_\pm = \pm aH + bH^2$ for the outer lines and $E_0 = b'H^2$ for the center line. The values of the coefficients are $a = (0.147\pm 0.003)$ cm^{-1}/kG, $b = (1.1\pm 0.1)\times 10^{-3}$ cm^{-1}/kG^2, and $b' = (0.29\pm 0.07)\times 10^{-3}$ cm^{-1}/kG^2. From the coefficient a we find that the P-state Zeeman mass (m_Z) is $(0.320\pm 0.007)\times m_e$. This is to be compared with the weak-field cyclotron mass (m_c) of $0.27m_e$.

To understand why the P-state Zeeman mass is larger than the weak-field cyclotron mass we first consider a crude but instructive variational calculation of the $2P$ hydrogenic levels in a magnetic field. In units of $\hbar\omega_{LO}$ and r_0, we write the Fröhlich Hamiltonian for an electron in a Coulomb potential and an external magnetic field as

$$H = H_0 + H_1 + H_2, \quad H_0 = -\nabla^2 - \beta/r + \sum b_{\vec{k}}^\dagger b_{\vec{k}},$$

$$H_1 = \frac{1}{2}\frac{\omega_{FL}}{\omega_{LO}} L_z + \frac{1}{16}\left(\frac{\omega_{FL}}{\omega_{LO}}\right)^2 (x^2+y^2),$$

$$H_2 = \sum v_k (e^{-i\vec{k}\cdot\vec{r}} b_{\vec{k}}^\dagger + e^{i\vec{k}\cdot\vec{r}} b_{\vec{k}}), \tag{1}$$

where ω_{FL} is the fixed-lattice cyclotron frequency $eH/m_{FL}c$, L_z is the angular-momentum operator, $\beta = 2(\mathrm{Ry}/\hbar\omega_{LO})^{1/2}$, $v_k = (4\pi\alpha r_0^3/V)^{1/2} 1/k$, and $\mathrm{Ry} = m_{FL}e^4/2\epsilon_0^2\hbar^2$.

In our experiment the magnetic field is weak compared with the Coulomb field ($\gamma = \hbar\omega_{FL}/2\mathrm{Ry} \sim 0.03$); so we can neglect mixing of the unperturbed eigenstates (eigenstates of H_0) due to H_1. Denoting $|0\rangle\Theta_{P\pm1}(\beta)$ and $|0\rangle\Theta_S(\beta)$ as normalized $2P_{\pm1}$ and $1S$ eigenfunctions, respectively, of H_0, where $|0\rangle$ is the LO-phonon vacuum, we expect that $|0\rangle\Theta_{P\pm1}(\beta)$ will be mixed most strongly with one-phonon $1S$ states of the form $b_{\vec{k}}^\dagger|0\rangle\Theta_S(\beta)$. This follows from the close proximity of the energy of these states to $|0\rangle\Theta_{P\pm1}(\beta)$. (Other one-phonon and multiphonon states lie much farther away from the zero-phonon P state.)

Thus we take as a crude trial function for the two $2P$ states transforming under rotation like $x \pm iy$

$$|0\rangle\Theta_{P\pm1}(\beta) + i\sum_{\vec{k}}(k_x \pm ik_y)s_k b_{\vec{k}}^\dagger|0\rangle\Theta_S(\beta), \tag{2}$$

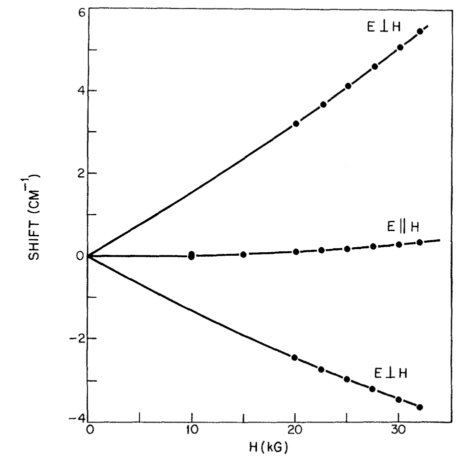

FIG. 2. Plot of the shifts of individual components of the "168-cm^{-1}" line from their zero-field value of 167.6 cm^{-1}. Dots are the experimental data. See text for explanation of solid curves.

where s_k is a real, spherically symmetric function to be determined variationally.

Denoting our variational $2P\pm1$ energies by $\lambda_{\pm1}$ we obtain after some computation

$$\lambda_{\pm1}(\omega_{FL}) = \frac{-\beta^2}{16} \pm \frac{\omega_{FL}}{2\omega_{LO}} + \frac{1}{2\beta^2}\left(\frac{\omega_{FL}}{\omega_{LO}}\right)^2 + \frac{C}{\lambda_\pm(\omega_{FL}) + \beta^2/4 - 1}, \tag{3}$$

where $C = 56\alpha\beta/6561$. Equation (3) gives two solutions for λ_{+1}, denoted by λ_{+1}^+ and λ_{+1}^-, and for λ_{-1}, denoted by λ_{-1}^+ and λ_{-1}^-; $\lambda_{\pm1}^+$ and $\lambda_{\pm1}^-$ lie, respectively, above and below $-\frac{1}{4}\beta^2 + 1$ at zero field. Since in the experiment we observe transitions to states well above the LO-phonon energy, we investigate here the Zeeman effect only in $\lambda_{\pm1}^+$. The ratio of the Zeeman mass to the fixed-lattice mass is $Z(\omega_{FL}) = \omega_{FL}/[\lambda_{+1}^+(\omega_{FL}) - \lambda_{-1}^+(\omega_{FL})]$. Expanding $\lambda_{\pm1}^+$ to order ω_{FL}/ω_{LO} we obtain

$$Z(0) = 1 + \frac{C}{[\lambda^+(0) + \beta^2/4 - 1]^2}. \tag{4}$$

Notice that $Z(0)$ is highly sensitive to the size of the resonant denominator in Eq. (4), that is, to the separation of the perturbed P-state energy from the ground-state energy plus one optical phonon ($-\frac{1}{4}\beta^2 + 1$). Thus m_Z can be very large.

We have produced a much better wave function than (2) by "dressing" the bare states $|0\rangle\Theta_{P\pm1}$ and $|0\rangle\Theta_S$ appearing there. Our dressed S state is simply the product-Ansatz state $U(F_k)|0\rangle\Theta_S(\beta + \frac{5}{8}\alpha)$; to dress our P state we have introduced

Table I. Comparison of experiment, refined theory [based on dressed wave function of Eq. (6)] and crude theory [bare wave function, Eq. (2)]. Here $h\nu_T$ is the zero-field transition energy and $D_{\pm1,0}$ is the diamagnetic (quadratic) Zeeman shift in the $1S$-to-$2P_{\pm1,0}$ transition energy at 30 kG. The experimental m_Z is an average of values obtained over the range 20-32 kG, while the theoretical values are computed at 30 kG.

	m_Z	m_c	m_{FL}	$h\nu_T$ (cm^{-1})	$D_{\pm1}$ (cm^{-1})	D_0 (cm^{-1})
Experiment	0.320 ± 0.007	0.27		167.63 ± 0.05	0.98 ± 0.05	0.31 ± 0.05
Theory [from Eq. (6)]	0.315	0.271	0.205	167.15	1.01	0.38
Theory [from Eq. (2)]	0.275	0.229	0.229	167.7	0.83	0.33

the novel dressing operator

$$O(h_k) \equiv \exp(-i\sum \vec{k} b_{\vec{k}}^\dagger b_{\vec{k}} \cdot \vec{r}) U(f_k) \times (1 + \sum h_k \vec{k} \cdot \vec{\pi} b_{\vec{k}}^\dagger), \qquad (5)$$

where

$$f_k = \frac{-\nu_k}{1+k^2}, \quad F_k = -\nu_k \left[\frac{1+k^2}{(\beta + 5\alpha/8)^2}\right]^{-2},$$

$$\vec{\pi} = (-i\partial/\partial x - \omega_c x/4\omega_{LO}, \ -i\partial/\partial y + \omega_c y/4\omega_{LO}, \ -i\partial/\partial z),$$

and for a function g_k, $U(g_k) = \exp[\sum g_k(b^\dagger_{\vec{k}} - b_{\vec{k}})]$. Thus our trial wave function is

$$\Phi_{P\pm1}(\beta_P) + i\sum(k_x \pm ik_y) s_k U(F_k) b_{\vec{k}}^\dagger |0\rangle \times \Theta_S(\beta + \tfrac{5}{8}\alpha), \qquad (6)$$

where $\Phi_{P\pm1}(\beta_P) = O(h_k)|0\rangle\Theta_{P\pm1}(\beta_P)$, h_k and s_k are spherically symmetric real functions determined variationally, and β_P is determined by minimizing for given h_k the expectation value $\langle\Phi_{P\pm1}|H \times|\Phi_{P\pm1}\rangle/\langle\Phi_{P\pm1}|\Phi_{P\pm1}\rangle$. A more complete discussion of (6) will be given in a future publication. We note that the effective-mass dressing operator given in (5), when operating on the zero-phonon Landau state $\Phi_n(r)|0\rangle$, produces a wave function which for weak magnetic fields yields a variational energy

$$-\alpha + \frac{(1-\alpha/12)}{(1+\alpha/12)}(n+\tfrac{1}{2})\frac{\omega_{FL}}{\omega_{LO}}.$$

Thus we obtain for the low-field cyclotron mass $m_c = (1+\alpha/12)(1-\alpha/12)^{-1} m_{FL}$ within the framework of our variational approximation.[8] We have computed not only m_Z/m_c but also the quadratic Zeeman shifts for (6) using an assumed $m_{FL} = 0.205$. Comparison of theory with experiment is given in Table I.

The remarkable agreement obtained from (6) is to some extent fortuitous since using a better ground-state trial function than our choice, $U(F_k)|0\rangle\Theta_S(\beta+\frac{5}{8}\alpha)$, would necessitate insertion of a short-range repulsive potential[3] into (1). Computer experimentation indicates that our calculated Zeeman mass would be little affected by a short-range potential whose strength is adjusted to maintain $1S$-$2P$ separation at $1.35\hbar\omega_{LO}$.

We remark that our computation gives a systematic shift downward in $Z(\omega_c)$ with increasing field. The shift is proportional to ω_c^2 and amounts to 2% at 30 kG. Our experimental results between 20 and 32 kG show a systematic shift upward in mass of about 2%, which lies barely outside of experimental error. This discrepancy is being investigated.

We have used the value $\hbar\omega_{LO} = 124$ cm^{-1} in fitting theory to experiment in the foregoing. This value agrees with (1) the phonon sideband separations of the $1S$-$2P$ transition identified by Brandt and Brown[3] and (2) the phonon sidebands seen in the indirect gap absorption[3]; it also gives the correct temperature dependence of the electronic mobility measured by Ahrenkiel.[9] On the other hand, the generally accepted value of $\hbar\omega_{LO}$ is 139 cm^{-1} in AgBr.[5] This latter value of $\hbar\omega_{LO}$ gives a Zeeman mass from (1) and (6) of $2.1m_c$, far larger than observed.

Perhaps the most tantalizing question left unanswered by the present work is how to account for the large discrepancy between the two values of the LO-phonon energy.

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[7]Our α is the conventional Fröhlich α given by

$$\frac{1}{2}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\frac{e^2}{r_0}\frac{1}{\hbar\omega_{\rm LO}},$$

where $r_0=(\hbar/2m_{\rm FL}\omega_{\rm LO})^{1/2}$, ϵ_∞ is the optical dielectric constant (4.62 ± 0.03) [A. Eucken and A. Büchner, Z. Physik. Chem. 27B, 321 (1934)], and $m_{\rm FL}$ is the fixed-lattice mass $(\approx 0.21m_e)$ corresponding to the cyclotron-resonance mass.

[8]This mass is, in fact, superior to the more commonly assumed Lee-Low-Pines mass $(1+\alpha/6)m_{\rm FL}$; see D. M. Larsen, Phys. Rev. 144, 697 (1966), and 174, 1046 (1968).

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