[1] E. A. Hylleraas and A. Ore, Phys. Rev. 71, 493 (1947).
[2] J. Adamowski, S. Bedanarek, and M. Suffczynski, Solid State Commun. 9, 2037 (1971).
[3] V. D. Kulakovskiĭ and V. B. Timofeev, Pis'ma Zh. Eksp. Teor. Fiz. 25, 487 (1977) [JETP Lett. 25, 458 (1977)].
[4] V. D. Kulakovskiĭ, V. B. Timofeev, and V. M. Édel'shteĭn, Zh. Eksp. Teor. Fiz. 74, 372 (1978) [Sov. Phys. JETP 47, 193 (1978)].
[5] P. L. Gourley and J. P. Wolfe, Phys. Rev. Lett. 40, 526 (1978).
[6] J. P. Wolfe, Proc. 14th Internat. Conf. Phys. Semicond., Edinburgh, 1978, p. 367.
[7] W. F. Brinkman, T. M. Rice, and B. Bell, Phys. Rev. B 8, 1570 (1973).
[8] G. L. Bir and G. E. Pikus, Simmetriya i deformatsionnye effekty v poluprovodnikakh (Symmetry and the Effects of Strain in Semiconductors), Nauka, 1972.
[9] I. Balslev, Phys. Rev. 143, 636 (1966).
[10] I. V. Alkeev, A. S. Kaminskiĭ, and Ya. E. Pokrovskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. 18, 671 (1973) [JETP Lett. 18, 393 (1973)].
[11] V. D. Kulakovskiĭ, I. B. Levinson, and V. B. Timofeev, Fiz. Tverd. Tela 20, 399 (1978) [Sov. Phys. Solid State 20, 230 (1978)].
[12] F. Merlet, B. Pajot, P. Arcas, and A. M. Jean-Louis, Phys. Rev. B 12, 3297 (1975).
[13] V. M. Asnin, G. L. Bir, Yu. N. Lomasov, G. E. Pikus, and A. A. Rogachev, Zh. Eksp. Teor. Fiz. 71, 1600 (1976) [Sov. Phys. JETP 44, 838 (1976)].
[14] P. D. Altukhov, G. E. Pikus, andA. A. Rogachev, Fiz. Tverd. Tela 20, 489 (1978) [Sov. Phys. Solid State 20, 283 (1978)].
[15] V. D. Kulakovshiĭ, A. V. Malyavkin, and V. B. Timofeev, Zh. Eksp. Teor. Fiz. 76, 272 (1979) [Sov. Phys. JETP 49, (1979)].
[16] G. L. Bir and G. E. Pikus, Proc. 7th Internat. Conf. Phys. Semicond., Dunod, Paris, 1964, p. 789.
[17] V. D. Kulakovskiĭ, V. B. Timofeev, and V. M. Édel'shteĭn, Proc. 14th Internat. Conf. Phys. Semicond., Edinburgh, 1978, p. 383.
[18] V. M. Édel'shteĭn, Zh. Eksp. Teor. Fiz. 77, 760 (1979) (next paper).
[19] S. T. Chui, Phys. Rev. B 9, 3438 (1974).

Translated by W. F. Brown, Jr.

Diamagnetic susceptibility of excitonic molecules

V. M. Édel'shteĭn

Institute of Solid State Physics, USSR Academy of Sciences

(Submitted 30 March 1978)
Zh. Eksp. Teor. Fiz. 77, 760–763 (August 1979)

Excitonic molecules in semiconductors in the presence of a magnetic field are considered. In the limit of equal isotropic masses of the electron and hole it is shown that the susceptibility of the molecule can exceed the susceptibility of two free excitons by not more than a factor of 1.9.

PACS numbers: 71.35. + z, 75.20. − g

Generalizing the exciton concept, Lampert[1] postulated the possible existence, in semiconductors, of various complexes consisting of a larger number of particles than the electron-hole pair. One such complex is a bound state of two electrons and two holes—the excitonic molecule (EM). If the effective masses of the electron and hole differ substantially, then the EM is equivalent to the hydrogen molecule. By contrast, the possibility of binding four particles with equal masses is less obvious. This problem, which is equivalent to the problem of the existence of the positronium molecule was finally solved by Hylleraas and Ore[3] by a variational method.

It has recently become possible to investigate EM in experiment. The most convincing proof of observing EM pertains to Si.[3-5] Although the electrons in Si have an isotropic mass, the average electron mass $m_e = (m_{e\perp}{}^2 m_{e\parallel})^{1/3} \approx 0,33 m_0$ is almost equal to the hole mass $m_h \approx 0,23 m_0$. Therefore the model of equal isotropic masses seems suitable for Si. We consider throughout just this limiting case. The degeneracy of the hole band is assumed lifted by external pressure.

It follows from Refs. 2 and 6, where a more successful trial wave function was proposed, that the molecule has a rather small binding energy $\Delta \approx 0.03 R_x$ where R_x is the exciton binding energy, and relatively large dimensions of order $3a_x$, where $a_x = 2\varepsilon_0 \hbar^2/me^2$ is the Bohr radius of the exciton. Two contradictory assumptions can be made here with respect to the value of the diamagnetic susceptibility χ_M of the molecule. On the one hand, in analogy with atoms, where according to Langevin the diamagnetic susceptibility is proportional to the square of the distance from the electron to the nucleus one might expect $\chi_M \sim 10\chi_x$, where χ_x is the diamagnetic susceptibility of the exciton. On the other hand, the low binding energy seems to indicate that the electron-hole correlations in the molecule are practically the same as in the exciton and therefore χ_M should not differ greatly from $2\chi_x$. The result of the present paper is the inequality

$$|\chi_M/2\chi_x| < 1.9. \tag{1}$$

The Hamiltonian of a molecule in a magnetic field is

$$\mathscr{H} = \frac{1}{2m}\left[\left(\mathbf{p}_1 + \frac{e}{c}\mathbf{A}_1\right)^2 + \left(\mathbf{p}_a - \frac{e}{c}\mathbf{A}_a\right)^2 + \left(\mathbf{p}_2 + \frac{e}{c}\mathbf{A}_2\right)^2 + \left(\mathbf{p}_b - \frac{e}{c}\mathbf{A}_b\right)^2\right] + V_{coul}, \tag{2}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the electrons, $\mathbf{r}_a$ and $\mathbf{r}_b$ are the coordinates of the holes, $\mathbf{A}_\mathbf{r} = 1/2\mathbf{H} \times \mathbf{r}$, and V_{coul} is the Coulomb-interaction potential. We have

0038-5646/79/080384-03$02.40

not written out here the interaction of the spins with the magnetic field, since this interaction is assumed to have no effect on the orbital motion.

The motion of the center of gravity of a molecule can be separated from the internal motions by Lamb's method.[7] Namely, the conserved total-momentum operator of the molecule is

$$\hat{\mathbf{K}}=\mathbf{p}_1+\mathbf{p}_2+\mathbf{p}_a+\mathbf{p}_b+\frac{e}{c}(\mathbf{A}_a+\mathbf{A}_b-\mathbf{A}_1-\mathbf{A}_2). \tag{3}$$

The eigenfunctions of the operator $\hat{\mathbf{K}}$, corresponding to the eigenvalue of $\mathbf{K}$ in terms of the coordinates

$$\mathbf{z}=\mathbf{r}_1-\mathbf{r}_a,\ \boldsymbol{\zeta}=\mathbf{r}_2-\mathbf{r}_b,\ \mathbf{R}={}^1/_2(\mathbf{r}_1+\mathbf{r}_a-\mathbf{r}_2-\mathbf{r}_b),\quad Q={}^1/_4(\mathbf{r}_1+\mathbf{r}_2+\mathbf{r}_a+\mathbf{r}_b), \tag{4}$$

take the form

$$\Phi_{\mathbf{K}}=\exp\left\{\frac{i}{\hbar}\left(\mathbf{K}+\frac{e}{c}\mathbf{A}_{\mathbf{z}+\boldsymbol{\zeta}}\right)Q\right\}\psi_{\mathbf{K}}(\mathbf{R},\mathbf{z},\boldsymbol{\zeta}). \tag{5}$$

Here $\psi_{\mathbf{K}}$ is an eigenfunction of the Hamiltonian

$$\mathscr{H}_{\mathbf{K}}=\frac{1}{8m}\mathbf{K}^2+\frac{e}{2mc}\mathbf{K}\mathbf{A}_{\mathbf{z}+\boldsymbol{\zeta}}+\mathscr{H}_0+\mathscr{H}_1+\mathscr{H}_2, \tag{6}$$

where

$$\mathscr{H}_0=\frac{1}{2m}\mathbf{P}_{\mathbf{R}}^2+\frac{1}{m}(\mathbf{p}_{\mathbf{z}}^2+\mathbf{p}_{\boldsymbol{\zeta}}^2)+V_{coul}$$

is the Hamiltonian of the molecule in the c.m.s. in the absence of a magnetic field,

$$\mathscr{H}_1=\frac{e}{mc}\left[(\mathbf{p}_{\mathbf{z}}-\mathbf{p}_{\boldsymbol{\zeta}})\mathbf{A}_{\mathbf{R}}+\frac{1}{2}\mathbf{P}_{\mathbf{R}}\mathbf{A}_{\mathbf{z}-\boldsymbol{\zeta}}\right], \tag{7}$$

$$\mathscr{H}_2=\frac{e^2}{mc^2}\left[\frac{3}{8}\mathbf{A}_{\mathbf{z}+\boldsymbol{\zeta}}^2+\frac{1}{2}\mathbf{A}_{\mathbf{R}}^2+\frac{1}{4}(\mathbf{A}_{\mathbf{z}}^2+\mathbf{A}_{\boldsymbol{\zeta}}^2)\right]. \tag{8}$$

The total momentum $\mathbf{K}$ of the molecules will henceforth be assumed equal to zero. The mean value of $\mathscr{H}_1$ on the functions of the ground state $\mathscr{H}_0$ is equal to zero from symmetry considerations. Therefore the energy correction, which is proportional to the square of the magnetic field, stems from $\mathscr{H}_1$ in second order of perturbation theory (the Van Vleck orbital paramagnetism) and from $\mathscr{H}_2$ in first order (the Langevin diamagnetism).

The form (5) of the Lamb transformation for a molecule is not unique, in contrast to the exciton. For example, to study the scattering of two excitons it is more convenient to use another gauge:

$$\psi_{\mathbf{K}}=\exp\left(-\frac{ie}{2\hbar c}\mathbf{R}\mathbf{A}_{\mathbf{z}-\boldsymbol{\zeta}}\right)\varphi_{\mathbf{K}}(\mathbf{R},\mathbf{z},\boldsymbol{\zeta}). \tag{5'}$$

We study first the contribution of $\mathscr{H}_2$ to the susceptibility χ_M. We note that the Hamiltonian $\mathscr{H}_0$ (just as $\mathscr{H}$) is invariant to the operation π of exchange of two electrons, which takes in the coordinates (4) the form

$$\pi(\mathbf{z},\boldsymbol{\zeta},\mathbf{R})=(\mathbf{z}',\boldsymbol{\zeta}',\mathbf{R}'), \tag{9}$$

where

$$\mathbf{z}'=-\mathbf{R}+(\mathbf{z}+\boldsymbol{\zeta})/2,\ \boldsymbol{\zeta}'=\mathbf{R}+(\mathbf{z}+\boldsymbol{\zeta})/2,\ \mathbf{R}'=(\boldsymbol{\zeta}-\mathbf{z})/2.$$

It follows from the fact that the wave function ψ of the ground state $\mathscr{H}_0$ is even relative to the π transformation that the Langevin correction to the energy is of the form

$$\delta E_L=\frac{e^2}{mc^2}\left[\frac{3}{4}(\langle A_{\mathbf{z}}^2\rangle+\langle A_{\boldsymbol{\zeta}}^2\rangle)+\frac{1}{2}\langle \mathbf{A}_{\mathbf{z}}\mathbf{A}_{\boldsymbol{\zeta}}\rangle\right]. \tag{10}$$

It is seen that δE_L does not reduce to the mean value of the square of any distance, as is the case for atoms.

Expression (10) can be simplified by averaging over the directions of the magnetic field and taking the symmetry $\mathbf{z}\leftrightarrow\boldsymbol{\xi}$ into account. We thus obtain

$$\delta E_L=\frac{e^2}{6mc^2}H^2\left[\frac{3}{2}\langle z^2\rangle+\frac{1}{2}\langle \mathbf{z}\boldsymbol{\zeta}\rangle\right]. \tag{11}$$

It is more convenient to calculate the integrals in terms of the variables first introduced by Hylleraas and Ore[2]:

$$s_1=r_{1a}+r_{1b},\ s_2=r_{2a}+r_{2b},\ v=r_{ab},\quad t_1=r_{1a}-r_{1b},\ t_2=r_{2a}-r_{2b},\ \phi, \tag{12}$$

where $r_{1a}=|\mathbf{r}_1-\mathbf{r}_a|$ etc., ϕ is the angle between the planes ($ab1$) and ($ab2$). For the wave function ψ we choose the trial function proposed earlier, which gives the highest binding energy of the molecules. In this case

$$\langle z^2\rangle/a_x^2=\frac{1}{k^5\|F\|^2}\int_0^\infty v^2\frac{F^2(v/k)}{N^2(v)}G_{z^2}(v)\,dv, \tag{13}$$

where

$$N^2(v)=\int_v^\infty ds_1\int_{-v}^{v}dt_1\frac{s_1^2-t_1^2}{4}\int_v^\infty ds_2\int_{-v}^{v}dt_2\frac{s_2^2-t_2^2}{4}\psi_{\text{MO}}^2\equiv\int\psi_{\text{MO}}^2\,d\mu; \tag{14}$$

$$\psi_{\text{MO}}=2\exp\left(-\frac{s_1+s_2}{2}\right)\cosh\left[\frac{\beta}{2}(t_1-t_2)\right],$$

$$F(v)=\frac{v}{A}e^{-v/A}+Ce^{-Bv/A},$$

$$\|F\|^2=\int_0^\infty F^2(v)v^2\,dv,\quad G_{z^2}(v)=\int\left[\frac{(s_1+t_1)^2}{4}\right]\psi_{\text{MO}}^2\,d\mu.$$

In the analogous expression for $\langle\mathbf{z}\boldsymbol{\zeta}\rangle/a_x^2$ it is necessary to replace the square bracket in the formula for G by $(s_1t_1+v^2)(s_2t_2-v^2)/4v^2$. Here $k=1.18$, $\beta=0.655$, $A=1.14$, $B=0.36$, $C=0.39$. The integrals (13) reduce to one-dimensional ones and can then be evaluated numerically. As a result we get

$$\langle z^2\rangle/a_x^2=10.0,\quad \langle \mathbf{z}\boldsymbol{\zeta}\rangle/a_x^2=7.2,\quad \langle v^2\rangle/a_x^2=9.9, \tag{15}$$

meaning that

$$\delta E_L=\frac{e^2}{6mc^2}H^2a_x^2\cdot 11.4. \tag{16}$$

For one exciton, the diamagnetic energy shift is

$$\delta E_x=\frac{e^2}{6mc^2}H^2a_x^2\cdot 3.$$

The Van Vleck paramagnetic shift is $\delta E_{vv}<0$, from which follows the estimate (1).

It appears at first glance that the first term of the sum over the intermediate states, which represents δE_{VV}, is anomalously large, since the denominator contains the low molecule binding energy $\Delta\ll R_x$. However, the matrix element $\mathscr{H}_1$ between the ground state of the molecule and of that dissociated into two uncexcited excitons vanishes because the ground-state functions of the molecule and of the exciton are invariant to rotations. The remaining energy denominators are of the order of R_x. It is assumed here also that in the case when the electron and hole masses are different there exists only one bound state of the molecules, i.e., there are no rotational or vibrational levels. We note also that $\mathscr{H}_1$ is invariant to the electron π-exchange transformation (9). It follows therefore that in the sum that represents δE_{VV} a nonzero contribution is made only by intermediate states that are even in π. The calculation of this sum calls for knowledge of all the excited states of the molecule, and is a difficult quantum-chemistry problem. In any case $|\chi_M|$ should apparently exceed $|2\chi_x|$. The inequality (1) then restricts quite strongly the possible value of χ_M.

Thus, the diamagnetic susceptibility of a molecule does not differ greatly from double the exciton susceptibility, even though the trial function (14) does not contain the wave functions of two excitons. It should be noted that the accuracy of the obtained inequality corresponds to the accuracy of the trial wave function (14).

The author thanks N. Tal'yanskaya for help with the numerical calculations and V. D. Kulakovskiĭ and V. B. Timofeev for a discussion of the experiments.

[1] M. Lampert, Phys. Rev. Lett. 1, 450 (1958).
[2] E. A. Hylleraas and A. Ore, Phys. Rev. 71, 493 (1947).
[3] V. D. Kulakovskiĭ and V. B. Timofeev, Pis'ma Zh. Eksp. Teor. Fiz. 25, 487 (1977) [JETP Lett. 25, 458 (1977)]; V. D. Kulakovskiĭ, V. B. Timofeev, and V. M. Édel'shteĭn, Zh. Eksp. Teor. Fiz. 74, 372 (1978) [Sov. Phys. JETP 47, 193 (1978)].
[4] P. L. Gourley and J. P. Wolfe, Phys. Rev. Lett. 46, 526 (1978).
[5] M. L. W. Thewalt, J. A. Rostorowski, Sol. St. Comm. 25, 991 (1978).
[6] W. F. Brinkman, T. M. Rice, and B. Bell, Phys. Rev. B8, 1570 (1973).
[7] W. E. Lamb, Phys. Rev. 85, 259 (1952).

Translated by J. G. Adashko

Antiferromagnetic resonance in hematite with Sn^{4+} impurity

B. Ya. Kotyuzhanskiĭ, M. Maryshko, and L. A. Prozorova

A. V. Shubnikov Institute of Crystallography, Academy of Sciences, USSR

(Submitted 10 April 1979)
Zh. Eksp. Teor. Fiz. 77, 764–772 (August 1979)

Antiferromagnetic resonance is studied in single crystals of α-Fe$_2$O$_3$ + 0.8 wt% Sn^{4+} over the temperature interval 1.2 to 300 K and the frequency range 23 to 70 GHz. It is found that the Morin point, if it exists, lies below 1.2 K. The temperature dependence of the parameters that determine the AFMR spectrum is investigated. It is found that the isotropic gap in the AFMR spectrum and the hexagonal anisotropy in the basal plane increase anomalously with lowering of the temperature. On cooling of the crystal in a magnetic field $H_0 \perp D_3$, there freezes into it at $T < 18 \pm 1$ K a uniaxial anisotropy with easy direction of the ferromagnetic vector $\mathbf{m}_0 \parallel \mathbf{H}_0$. A theoretical investigation is made of a mechanism based on the formation of bound states Fe^{2+}–Sn^{4+}, which lead, because of distortion of the local crystalline field on the Fe^{2+} ions, to the inducing of additional anisotropy in the crystal. It is shown that this mechanism describes all the observed effects.

PACS numbers: 76.50. + g, 75.30.Gw, 75.50.Bb

Hematite, α-Fe$_2$O$_3$, is a well studied antiferromagnetic material with $T_N = 970$ K. It is known that at temperature $T_M = 263$ K (the Morin point), a phase transition occurs in hematite, from an easy-plane weakly ferromagnetic state at $T > T_M$ to an easy-axis antiferromagnetic state at $T < T_M$. Investigations of the static magnetic properties,[1] of the Mössbauer effect,[2] and of neutron diffraction[3] have shown that upon introduction into hematite of small quantities (~1%) of metallic impurity (Al, Ti, Sn, etc.), the Morin point changes. It follows from these researches that the greatest effect on the Morin point is caused by introduction into hematite of tetravalent tin.

The present paper is devoted to a study of antiferromagnetic resonance (AFMR) over a broad temperature range in hematite that contained 0.8 wt% Sn^{4+}. As an NMR study has shown,[4] in this case the Morin point is substantially lowered: $T_M < 77$ K. The AFMR method was chosen because it is very sensitive to change of the magnetic structure and enables one to determine a number of magnetic constants.

METHOD AND SPECIMENS

AFMR in hematite was studied on a direct-amplification magnetic spectrometer. A shorted waveguide served as the measurement cell; the specimen was placed on its copper cap, at an antinode of the microwave magnetic field. In order that elastic stresses should not occur in the specimen on cooling, it was not cemented to the waveguide cap but was lightly attached to it with a stopper of foam plastic. The resonance absorption line was recorded with an xy recorder, which registered the change of the microwave signal reflected from the crystal as a function of the value of the magnetic field H. The magnetic field was produced by a laboratory electromagnet and was measured with a Hall detector with accuracy 1%.

The measurements were made over the frequency range 23 to 70 GHz and over the temperature interval 1.2 to 300 K. Temperatures below 4.2 K were obtained by evaporation of liquid helium; above, by use of a vacuum cryostat similar to that described in Ref. 5.