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Abstract

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THE PARAMAGNETIC COMPONENT OF THE MAGNETIC SUSCEPTIBILITY OF SEMICONDUCTOR CRYSTALS FROM EXPERIMENTAL DATA ON THE ELECTRON-DENSITY DISTRIBUTION

We have previously shown the possibility of determining the diamagnetic component of the magnetic susceptibility of semiconductor crystals from data on the electron density determined experimentally by X-ray diffraction or neutron diffraction methods ([1]). However, as is known ([2–5]), in the majority of diamagnetic crystals, along with the diamagnetic component of the magnetic susceptibility, one must also take into account a paramagnetic component, whose absolute value is of the same order as that of the diamagnetic component. The resulting magnetic susceptibility of diamagnetic crystals is thus, as a rule, determined by the difference of quantities that are close in order of magnitude.

According to the quantum-mechanical theory of diamagnetism ([5]), the magnetic susceptibility of many-atom systems consists of two terms—the Langevin term, which determines the diamagnetic component χ_d, dependent on the mean square radius of the electronic orbits, and the Van Vleck term, which has the opposite sign and determines the paramagnetic component of the magnetic susceptibility χ_p:

$$\chi = \chi_d + \chi_p = -\frac{Ne^2}{6mc^2}\sum_n \overline{r_n^2} + 2N\sum_{k\neq l}\frac{|_kM_l|_z^2}{E_l^0 - E_k^0}, \tag{1}$$

where $|_kM_l|_z$ is the off-diagonal matrix element of the z-component of the orbital magnetic moment along a certain axis z, coinciding with the direction of the magnetic field H; $E_l^0 - E_k^0$ is the energy difference between the ground nondegenerate state k and the excited state l. The summation is carried out over all possible states. In the case of semiconductors ([2,6]), the average value $\overline{E_l - E_k}$ may be equated to the width of the forbidden band ΔE.

The paramagnetic component of the magnetic susceptibility for electron clouds possessing spherical symmetry is zero. Owing to this circumstance, for purely ionic compounds with spherical ions and a small degree of polarization, the diamagnetic susceptibility is practically additively composed of the susceptibilities of the ions. In the case, however, of ionic compounds with a large polarization coefficient, semiconductor and covalent compounds, in which there is nonsphericity in the distribution of the electron density of the ions, overlap of the ion clouds, and formation of electronic "bridges" leading to asymmetry of the electron-density distribution, as well as deformation of the ions, the magnitude of the Van Vleck term becomes appreciable and, generally speaking, may be close to the magnitude of the diamagnetic component or even exceed it.

Up to the present time there have not existed sufficiently reliable experimental and theoretical quantitative or semiquantitative methods for separating the magnetic susceptibility into diamagnetic and paramagnetic components. The diamagnetic component can, with known accuracy, be estimated theoretically or determined from X-ray data.

analysis (^{1}). However, the most difficult task is the independent determination of the paramagnetic component, the importance of which was especially emphasized by Ya. G. Dorfman (^{2}).

In the present article we draw attention to the fundamental possibility of determining the paramagnetic component from experimental data on the distribution of electron densities in crystals.

In covalent, semiconducting, and partly ionic crystals, the electron clouds of ions in many cases do not possess spherical symmetry, and the clouds of neighboring atoms (ions) form regions of partial overlap. In this case there is also some deformation of the electron clouds of ions, leading to their deviation from sphericity. Nonspherical ions and regions of overlap for surfaces of equal electron densities may be approximately characterized as certain ellipsoids of revolution, while overlap regions, in the general case, as dumbbells. The edges of the dumbbells are diffuse. The electron density of a dumbbell ρ_n may be approximated by the sum of two functions characterizing the distribution of the electron density of the electrons of neighboring ions (atoms) participating in the formation of the bond:

$$\rho_n = \rho_A + \rho_B.$$

For an analytical approximation of the distribution of the electron density of ions and overlap regions, functions of the form

$$\rho = A \exp\left[-\sqrt{\alpha x^2 + \beta y^2 + \delta z^2}\right],$$

three-dimensional Gaussian distributions (^{7,8}), or functions of the type

$$\frac{A}{1+\alpha x^2+\beta y^2+\delta z^2}, \qquad \frac{A}{(1+\alpha x^2+\beta y^2+\delta z^2)^2}$$

and so forth may be chosen.

For example, the distribution of the electron density of an ion may be described as

$$\rho_A = A\exp\{-[\alpha x^2+\beta y^2+\delta z^2]\},$$

and for the overlap region of two identical atoms one may write

$$\rho_n = B\exp\{-[\gamma x^2+\beta y^2+\delta z^2]\}\left(\exp\left[-\frac{\gamma R}{2}\right]+\exp\left[\frac{\gamma R}{2}\right]\right).$$

Assuming that in cross section the dumbbell is round, one may put $\beta=\delta$. The quantities B and β are determined directly from the data of the map of the electron-density distribution in the overlap region (in the electron “bridge”).

From the condition of equality $\int \rho_n dv = n$, the number of electrons of the atoms participating in the bond, the value of the coefficient γ is found. Since the square of the wave function is proportional to the electron density $|\psi^2|=\rho$, the experimental map of the electron-density distribution may essentially be regarded as an experimental expression for the wave function, on the basis of which its analytical approximation can also be obtained.

Substituting the experimentally found expression for the wave function into the Van Vleck term of relation (1), we determine the paramagnetic component. Thus, using the quantum-mechanical mathematical apparatus and the experimentally found wave function, we obtain the value χ_p.

In relation (1), the square of the operator of the z-component of the magnetic moment may be defined as the product of the square of the Bohr magneton μ_B by the square of the angular-momentum operator:

$$|M_z|^2 = -\mu_B^2\left|y\frac{\partial}{\partial x}-x\frac{\partial}{\partial y}\right|^2. \tag{2}$$

Taking into account that, for example, in the diamond structure there are four bonds ($z=4$), mutually arranged at an angle for which $\cos\frac{\varphi}{2}=\frac{1}{\sqrt{3}}$, the obtained value of the susceptibility per one bridge must be multiplied by 8/3.

Then the expression for the paramagnetic component for cubic structures takes the form

$$\chi_p = -\frac{8}{3}\frac{N\mu_B^2}{\Delta E}\iiint\left[\left(y^2\frac{\partial^2\rho}{\partial x^2} - 2xy\frac{\partial^2\rho}{\partial x\,\partial y} + x^2\frac{\partial^2\rho}{\partial y^2}\right) - \frac{1}{2\rho}\left(y\frac{\partial\rho}{\partial x} - x\frac{\partial\rho}{\partial y}\right)^2 - \left(y\frac{\partial\rho}{\partial y} + x\frac{\partial\rho}{\partial x^2}\right)\right]dx\,dy\,dz.$$

In the absence of the possibility of approximating ρ_n by some analytic function, the integral can be determined by numerical integration from the data on the electron-density distribution of the electrons responsible for the bonds. Construction of these maps can be carried out, for example, by the method of separating the bond electrons from the inner shell (^{9}).

Calculation of the paramagnetic component for diamond from the electron-density distribution data (^{11}), computed from the f-curves determined by Brill et al. (^{10}), gives the value *

$$\chi_p = 0.6 \cdot 10^{-6}.$$

For the diamagnetic component, from the electron-density data we obtained (^{1})

$$\chi_d = -6.8 \cdot 10^{-6}.$$

The resulting total value is

$$\chi = \chi_d + \chi_p = -6.2 \cdot 10^{-6}.$$

The experimental value (^{12}) is

$$\chi = -5.9 \cdot 10^{-6}.$$

Determination of the diamagnetic and paramagnetic components from the data of X-ray or electron-diffraction measurements undoubtedly opens up new possibilities and is of considerable interest.

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CITED LITERATURE

1. N. N. Sirota, DAN, **142**, No. 6, 1278 (1962).
2. Ya. G. Dorfman, *Diamagnetism and the Chemical Bond*, Moscow, 1961.
3. Ya. G. Dorfman, ZhETF, **35**, 535 (1958).
4. C. Kittel, *Introduction to Solid State Physics*, 2nd ed., N. Y., 1956.
5. J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford, 1932.
6. J. A. Krumhause, H. Brooks, Bull. Am. Phys. Soc., **1**, 117, F. 5 (1956).
7. E. S. Wentzel, *Probability Theory*, Moscow, 1958.
8. B. V. Gnedenko, *Probability Theory*, Moscow, 1961.
9. G. B. Carpenter, J. Chem. Phys., **32**, No. 2, 525 (1960).
10. H. G. Grimm, R. Brill, C. Hermann, C. Peters, Ann. Phys., **34**, 393 (1939).
11. N. N. Sirota, N. M. Olekhnovich, A. U. Sheleg, DAN, **132**, No. 1, 160 (1960).
12. G. A. Bush, R. Kern, Helv. phys. acta, **32**, No. 1, 24 (1959).

* Allowance for the forbidden reflection (222) leads to somewhat smaller values of χ_t.

Note: Figure translations are in progress. See original paper for figures.

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