Physics

Academician of the Academy of Sciences of the BSSR N. N. Sirota

1962

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Abstract

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EXPERIMENTALLY DETERMINED DISTRIBUTION OF ELECTRON DENSITY IN CRYSTALS AND DIAMAGNETIC SUSCEPTIBILITY

An X-ray study of the distribution of electron density in crystals of simple substances and the simplest compounds makes it possible, with a known approximation, to give a quantitative estimate of the magnitude of the diamagnetic component of the magnetic susceptibility. In the present article we shall consider this question semi-quantitatively, with the aim of obtaining certain criteria for determining the diamagnetic susceptibility of crystals of simple substances and the simplest semiconductor compounds from X-ray structural-analysis data.

As is known, the gram-atomic diamagnetic susceptibility of a simple solid may be determined as a quantity proportional to the sum of the mean squares of the radii of the orbits of all electrons of charge e and effective mass m:

$$\chi_A = -\frac{Ne^2}{6mc^2} \sum_z \overline{r_i^2} \tag{1}$$

or

$$\chi_A = -2.829 \cdot 10^{10} \sum_z \overline{r_i^2}. \tag{2}$$

Thus, the problem of determining the diamagnetic susceptibility is reduced first of all to determining the sum of the mean values of the squares of the radii of the orbits of all electrons. $\sum_z \overline{r_i^2}$ may be determined as the product of the number of electrons by the mean square radius of the electron shell of the scattering atom:

$$\sum_z \overline{r_i^2} = z\,\overline{r^2}_{\text{av. at}} \tag{3}$$

As is known ([1]), for spherical ions the atomic scattering factor f_A is determined by the function of the radial distribution of electrons $U(r)$ and by the function of the scattering angle $\mu = 4\pi \sin\vartheta/\lambda$:

$$f_A = \int_0^\infty U(r) \frac{\sin \mu r}{\mu r} \, dr. \tag{4}$$

Since

$$\int_0^\infty U(r) \, dr = z,$$

then, on the basis of the mean-value theorem,

$$\overline{r^2} = \frac{1}{z} \int_0^\infty U(r) \, r^2 \, dr. \tag{5}$$

On the other hand, since $U(r) = 4\pi r^2 \rho(r)$, where ρ is the electron density at the point x, y, z, the mean square radius of the electron shell of the scattering atom will be determined through the electron density:

$$\overline{r^2} = \frac{4\pi}{z} \int_0^\infty \rho r^4 \, dr. \tag{6}$$

In this case the diamagnetic susceptibility can be expressed as a function of the electron density

$$\chi_A = -\frac{4\pi e^2 N}{6mc^2} \int_0^\infty \rho(r) r^4 \, dr = -35.556 \cdot 10^{10} \int_0^\infty \rho(r) r^4 \, dr. \tag{7}$$

Here attention is drawn to the circumstance that under the integral sign in (7) there is the radius to the fourth power, which indicates the considerable influence of the outer electrons on the diamagnetic susceptibility.

Using the Fourier transform, the mean square radius of the electron shell can be expressed in terms of the atomic scattering factor; consequently, the diamagnetic susceptibility can be expressed directly through the values of the intensities of X-ray scattering from various crystallographic planes (hkl) of crystals.

The distribution of the electron density in the crystal lattice of a solid monatomic body can, as is customary ([2]), be divided into at least two parts: $\rho = \rho_1 + \rho_2$. The greater part of the electrons, located mainly near the centers of the ion nuclei, can be described by a Gaussian distribution function $\rho_1 = Ae^{-\alpha r^2}$. The remaining part of the electrons, located predominantly in the outer part of the electron shell of the atoms and in the space between the ions, is described by the function ρ_2, which is determined from experimental data as the difference between the actual ρ and the prescribed ρ_1 distributions of electron density. Accordingly, the diamagnetic susceptibility of the crystal can be divided into two parts: χ_1, determined by the prescribed Gaussian distribution of electrons, and χ_2, by the above-mentioned distribution ρ_2:

$$\chi = \chi_1 + \chi_2. \tag{8}$$

In this case

$$\chi_1 = -\frac{4\pi e^2 AN}{6mc^2} \int_0^\infty e^{-\alpha r^2} r^4 \, dr = -23.6 \cdot 10^{-6} \frac{A}{\alpha^{5/2}}. \tag{9}$$

The quantities A and α are determined experimentally from the intensities of the lines $(h_1 k_1 l_1)$ and $(h_2 k_2 l_2)$ at sufficiently large values of the sums $h^2+k^2+l^2$, for example, greater than 25 ([2]).

In practice, the quantities α and A can be determined from the slope of the straight-line portion of the curve $\ln f$ as a function of the sum of the squares of the indices $\sum_i h_i^2$:

$$\alpha = \frac{\pi^2}{a^2 \operatorname{tg} \varphi}, \tag{10}$$

$$A = \frac{f_1(0)}{(\operatorname{tg} \varphi)^{3/2}} \frac{\pi^{3/2}}{a^3}, \tag{11}$$

where $\operatorname{tg} \varphi$ is the tangent of the slope of the curve $\left(\ln f, \sum_i h_i^2\right)$; a is the lattice constant; $f_1(0)$ are the values of f_1 for the rectilinear portion of the curve $\left(\ln f, \sum_i h_i^2\right)$, extrapolated to $\sum_i h_i^2 = 0$.

Using relations (10), (11), the quantity χ_1 can be expressed directly in terms of $\operatorname{tg} \varphi$, a, and $f_1(0)$:

$$\chi_1 = 0.429 \, f_1(0) \, a^2 \operatorname{tg} \varphi \cdot 10^{-6}. \tag{12}$$

χ_1 is the diamagnetic susceptibility of ions of spherical form, in which the radial distribution of the electron density, or, what is the same thing, of the square of the wave function, is described by an expression of Gaussian type

$$|\psi|^2 = 4\pi A r^2 e^{-\alpha r^2}. \tag{13}$$

Apparently, in most cases this function, extrapolated to zero temperature, is characteristic of the ions of a given simple substance in various compounds, remaining practically unchanged.

From this point of view, the quantity χ_2 depends to a substantially greater degree on the type of crystal lattice and may, as a rule, be regarded as depending to a greater extent on the type, features, and energy of the chemical interatomic bond.

Unlike χ_1, the quantity χ_2 is calculated directly from the experimental data of X-ray structural analysis as a quantity proportional to $r^4\rho_2$:

$$\chi_2 = -\frac{4\pi e^2 N}{6mc^2}\sum_i r_i^4 \rho_{2i}\Delta r = -\frac{4\pi e^2 N}{6mc^2}\sum_i r_i^4 \sum\sum\sum F_2 \exp[-2\pi i r \overline{H}]\,\Delta r. \tag{14}$$

Here the quantity F_2 is determined from the difference between the experimentally determined structure amplitude and the curve calculated for a specified value of f_1, with a known electron distribution.

Consequently, from the X-ray structural analysis data the values of A, α are determined, and the quantity χ_2 is calculated. Remaining within the approximation of spherical ions that partially overlap, it is relatively simple to estimate the values of χ_1 and χ_2 from experimental data on electron-density distributions. For example, the data given in ([2]) on the electron-density distribution for diamond make it possible to determine the values of A and α: $A = 157.22$ el/Å^3 and $\alpha = 66.42$ Å^{-2}. In this case, the molar diamagnetic susceptibility will be equal to

$$\chi_1 = -0.085 \cdot 10^{-6}.$$

The distribution of the electron density ρ_2 in the diamond lattice, from which the electron-density plots were constructed in work ([2]), is given in Table 1; the values of the products $\rho_2 r^4$ are also given there.

Table 1

Nos. of layers through 1/60 of the lattice constant	r^4, Å^4	ρ_2, $\frac{\text{el}}{\text{Å}^3}$	$\rho_2 r^4$	Nos. of layers through 1/60 of the lattice constant	r^4, Å^4	ρ_2, $\frac{\text{el}}{\text{Å}^3}$	$\rho_2 r^4$
0	0	3.16	0	8	0.4604	0.60	0.2716
1	0.0006	3.06	0.0003	9	0.7375	0.40	0.2950
2	0.0018	2.82	0.0051	10	1.1243	0.23	0.2586
3	0.0091	2.49	0.0227	11	1.6458	0.14	0.2304
4	0.0288	2.14	0.0616	12	2.3311	0.05	0.1165
5	0.0703	1.64	0.1153	13	2.8422	0.02	0.0568

Nos. of layers through 1/60 of the lattice constant	r^4, Å^4	ρ_2, $\frac{\text{el}}{\text{Å}^3}$	$\rho_2 r^4$	Nos. of layers through 1/60 of the lattice constant	r^4, Å^4	ρ_2, $\frac{\text{el}}{\text{Å}^3}$	$\rho_2 r^4$
6	0.1457	1.24	0.1807	14	4.3189	0.00	0.0000
7	0.2699	0.89	0.2402				

Summing the diamagnetic susceptibility layer by layer, using expression (14), we obtain the value of the diamagnetic susceptibility χ_2. The calculated value of the diamagnetic susceptibility proves to be $\chi_2 = -6.77 \cdot 10^{-6}$, and the total diamagnetic susceptibility, referred to the gram-atom, is

$$\chi = \chi_1 + \chi_2 = -6.85 \cdot 10^{-6}.$$

The experimental values of the diamagnetic susceptibility are $\chi_{\text{exp}} = -5.9 \cdot 10^{-6}$ ([3]). The theoretical calculation gives $\chi_{\text{theor}} = 6.8 \cdot 10^{-6}$ ([3]).

The discrepancy between the values calculated from the electron-density distribution and the experimental values may be due, among other things, also to the fact that the experimental integral values include a paramagnetic component of the magnetic susceptibility, which is not taken into account either in theoretical calculations or in calculations from experimentally determined values of the electron-density distribution.

In the approximation of spherical ions it appears possible to estimate the diamagnetic susceptibility of compounds from experimental data on the distribution of electron density in their lattice. For example, according to the data of work ([4]), for GaSb the values are $A_{\text{Ga}} = 277.014$, $\alpha_{\text{Ga}} = 15.972$, $A_{\text{Sb}} = 368.697$, $\alpha_{\text{Sb}} = 12.581$, $a = 6.087$ Å, $f_{1\text{Ga}}(0) = 24.19$, $\text{tg}_{\text{Ga}}\,\varphi = 0.0167$, $f_{1\text{Sb}}(0) = 46.07$, $\text{tg}_{\text{Sb}}\,\varphi = 0.0212$. Hence, on the basis of relations (10), (11), (12):

$$\chi_{1\text{Ga}} = -6.4 \cdot 10^{-6}, \quad \chi_{1\text{Sb}} = 15.5 \cdot 10^{-6}, \quad \chi_{1\text{GaSb}} = \frac{\chi_{1\text{Ga}} + \chi_{1\text{Sb}}}{2} = 11.0 \cdot 10^{-6}.$$

From the layer-by-layer values of the electron-density distribution in the lattice of the compound GaSb, the values of the products $\rho_2 r^4$ and of the diamagnetic susceptibility are calculated correspondingly for the Ga and Sb ions.

Summing layer by layer the diamagnetic susceptibility of the electron shells of the Ga and Sb ions by means of relation (14), we obtain the values of the diamagnetic susceptibility χ_2 of the Ga and Sb ions: $\chi_{2\text{Ga}} = -33.7 \cdot 10^{-6}$, $\chi_{2\text{Sb}} = -27.8 \cdot 10^{-6}$, whence for a gram-atom of the compound GaSb

$$\chi_{2\text{GaSb}} = \frac{\chi_{2\text{Ga}} + \chi_{2\text{Sb}}}{2} = -30.7 \cdot 10^{-6}.$$

The diamagnetic susceptibility of a gram-atom of the compound will be equal to the sum

$$\chi_{\text{GaSb}} = \chi_{1\text{GaSb}} + \chi_{2\text{GaSb}} = -41.7 \cdot 10^{-6}.$$

Calculating directly from the f-curve, using the repeated-logarithmization method f_2 [(5)], we obtain the value $\chi_{\text{GaSb}} = -38.7 \cdot 10^{-6}$.

The experimental data are $\chi_{\text{GaSb ion}} = -11.0 \cdot 10^{-6}$, $\chi_{\text{GaSb}} = -19.2 \cdot 10^{-6}$ [(3)]; the theoretical value is $\chi_{\text{theor GaSb}} = -30.35 \cdot 10^{-6}$ [(3)]. The values calculated from X-ray structural analysis data are substantially closer to the theoretical ones than to the values determined directly from magnetic measurements. The discrepancy with magnetic-measurement data may be due, among other things, to neglect of the paramagnetic component of the magnetic susceptibility. The indicated discrepancies are of considerable interest and require further investigation.

From electron-density maps in the lattices of simple substances and the simplest compounds it is possible to calculate not only the integral diamagnetic susceptibility, but also to take into account its anisotropy from the deviation of the electron distribution from spherical symmetry.

From X-ray structural-analysis data it is also possible to estimate the temperature dependence of the diamagnetic component of the magnetic susceptibility of crystals by measuring the intensities of reflections at various temperatures. Of considerable interest are the values of χ obtained by extrapolation to absolute zero temperature.

Since the quantity χ is a function of f, a, $\operatorname{tg}\varphi$, in order to determine the temperature coefficient $d\chi/dT$ it is necessary to find the temperature derivatives of these quantities. Analysis shows that the temperature coefficient of the diamagnetic susceptibility is, among other things, a function of the mean-square displacements $\overline{u^2}_{S,T}$ of the characteristic temperatures. The diamagnetic susceptibility is also a function of the mean-square static displacements $\overline{u^2}_{S,C}$.

Department of Solid-State and Semiconductor PhysicsAcademy of Sciences of the BSSR

Received11 X 1961

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1. P. James, *Optical Principles of the Diffraction of X-rays*, IL, 1950.

2. N. N. Sirota, N. M. Olekhnovich, A. U. Sheleg, DAN, **132**, No. 1, 160 (1960).

3. G. A. Bush, R. Kern, Helv. Phys. Acta, **32**, No. 1, 24 (1959).

4. N. N. Sirota, E. M. Gololobov, DAN, **138**, No. 1, 162 (1961).

5. R. Hosemann, G. Schoknecht, Zs. Naturforsch., **12a**, 932 (1957).

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