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1963

SovietRxiv

Abstract

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PHYSICS

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X-RAY DETERMINATION OF THE DIAMAGNETIC SUSCEPTIBILITY OF CERTAIN IONIC AND SEMICONDUCTOR COMPOUNDS

The experimentally determined lattice magnetic susceptibility χ of ionic and semiconductor compounds and other many-atom systems can be represented as the sum of two terms—the diamagnetic component (Langevin term) χ_d and the paramagnetic component (Van Vleck term) χ_p:

$$\chi = \chi_d + \chi_p = -\frac{Ne^2}{6mc^2}\sum_i \overline{r_i^2} + \frac{2}{3}N\sum_{j\neq i}\frac{|M(j,i)|^2}{E_j - E_i}, \tag{1}$$

where $M(j,i)$ is the off-diagonal matrix element of the magnetic moment; $E_j - E_i$ is the width of the forbidden band (gap); $\sum_i \overline{r_i^2}$ is the sum of the mean squares of the radii of the electron orbits. The first term is determined by the distribution of electron density in the lattice of the compounds; the second term, by the deviation of the electron-density distribution from sphericity.

As Ya. G. Dorfman emphasizes ([1]), it is of considerable interest to find independent ways of separating the experimentally determined magnetic susceptibility χ into the components χ_d and χ_p. It is known ([2]) that the diamagnetic component of the lattice susceptibility (the Langevin term) can be determined from data on the distribution of electron density, determined experimentally by the x-ray method.

The aim of the present investigation was to determine the diamagnetic component of the magnetic susceptibility of the arsenides and antimonides of aluminum, gallium, and indium from data on the distribution of electron densities in the lattice of these compounds obtained in our laboratory ([3–8]), and of the compounds NaCl, KCl, CaF_2, and Cu_2O, using literature data [(NaCl, KCl)([9]), (CaF_2)([10]), (Cu_2O)([11])].

The magnitude of the diamagnetic component was determined, in accordance with the method described earlier ([2]), using for each kind of ion the relation

$$\chi = -\frac{4\pi N e^3}{6mc^2}\int_0^\infty (\rho_1' + \rho_2')r^4\,dr = -23.64\cdot 10^{-6}\frac{A_1}{a_1^{5/2}} - 35.55\cdot 10^{10}\sum_i \rho_{2i}' r_1^4\cdot \Delta r, \tag{2}$$

where $\rho_1' = A_1 e^{-\alpha_1 r^2}$; ρ_2' was determined from the series $\sum_h \sum_k \sum_l F_2 \exp(-2\pi i \bar{r}\bar{H})$; F_2 was determined from the difference between the experimentally determined structure amplitude and the structure amplitude calculated for a given distribution of electron density $\rho_1 = \sum_i A_i e^{-\alpha_i (r-r_{0i})^2}$. The quantities A and α were determined experimentally from the logarithm of the f-curves in the region of the linear portion at comparatively large values of $\sum_i h_i^2$.

Since the temperature-independent diamagnetic component of the lattice susceptibility is being considered, the calculation was carried out by extrapolating the electron-density distribution to zero temperature for the ion at rest, also eliminating zero-point vibrations.

The quantities A_{01} and α_{01}, characterizing the distribution ρ_1' in the case of an ion at rest, are related to A_1 and α_1, determined at temperature T, by the relations

$$\alpha_{01} = \frac{\alpha_1}{1 - 2u_T^2\alpha_1}; \tag{3}$$

$$A_{01} = A_1 \frac{\alpha_{01}^{3/2}}{\alpha_1^{3/2}}. \tag{4}$$

The extrapolation of ρ_2' to absolute zero was also carried out with allowance for the temperature factor. However, as calculations and direct experiments have shown, the effect of temperature on the electron-density distribution ρ_2 and, correspondingly, on χ_2 is negligibly small.

Table 1

Diamagnetic component of the magnetic susceptibility of NaCl, KCl, CaF_2, and Cu_2O, determined from X-ray data

Compound	Ion	$-\chi_d \cdot 10^6$ per g-atom	$-\chi_d \cdot 10^6$ per mole	$-\chi_{\text{expt}} \cdot 10^6$ ([13])	$-\Delta\chi \cdot 10^6 = -(\chi_d - \chi_{\text{expt}}) \cdot 10^6$
NaCl	Na	5.0	30.7	30.3	0.4
NaCl	Cl	25.7	30.7	30.3	0.4
KCl	K	14.8	41.1	39.0	2.1
KCl	Cl	26.3	41.1	39.0	2.1
CaF_2	Ca	11.8	29.6	28.0	1.6
CaF_2	2F	17.8	29.6	28.0	1.6

Compound	Ion	$-\chi_d \cdot 10^6$ per g-atom	$-\chi_d \cdot 10^6$ per mole	$-\chi_{\text{expt}} \cdot 10^6$ ([13])	$-\Delta\chi \cdot 10^6 = -(\chi_d - \chi_{\text{expt}}) \cdot 10^6$
Cu_2O	2Cu	32.0	41.6	36.0	5.6
Cu_2O	O	9.6	41.6	36.0	5.6

Table 1 gives the results of calculating the diamagnetic susceptibility of the indicated ionic compounds.

It should be noted that, in determining the electron density, the error is of the order of 0.05 el/Å^3. This leads to an error in the determinations of the diamagnetic susceptibility of about 5%, i.e., of the same order as the accuracy of direct experimental measurements.

On the basis of analysis of the results presented in Table 1, it may be concluded that the diamagnetic susceptibility calculated from X-ray measurements for ionic compounds agrees well with the experimental values, which is due to the smallness of the paramagnetic component in the case of ionic compounds. This, in turn, makes it possible to regard the method for determining the diamagnetic component of the magnetic susceptibility from X-ray data as a sufficiently reliable independent method. When there are significant differences between the experimental values and those calculated from X-ray data, it may be assumed that the difference is determined mainly by the magnitude of the paramagnetic component (the Van Vleck term).

Table 2 gives the results of determining the diamagnetic susceptibility of compounds $A^{\text{III}}B^{\text{V}}$ with the sphalerite structure—arsenides and antimonides of aluminum, gallium, and indium (ΔE is the forbidden-band width; the quantity M_{01} was calculated from the values of $\Delta\chi$ and ΔE).

It follows from Table 2 that the difference $\Delta\chi$ between the experimental values and the values determined from X-ray data, corresponding to the paramagnetic component of the magnetic susceptibility,

significantly exceed the possible experimental errors. Thus, determination of the diamagnetic component from X-ray data makes it possible to separate the lattice magnetic susceptibility of the simplest compounds into χ_d and $\chi_p = \Delta\chi$.

Table 2

Diamagnetic component of the magnetic susceptibility of arsenides and antimonides of aluminum, gallium, and indium, determined from X-ray data
(experimental and theoretical values)

Compound	Ion	d, Å	$-\chi_d \cdot 10^6$ from X-ray data per g-atom	$-\chi_d \cdot 10^6$ from X-ray data per mole	$-\chi_{\text{exp}} \cdot 10^6$ ([13])	$-\chi_{d,\text{theor}} \cdot 10^6$ ([13])	$-\chi_d \cdot 10^6$ from polarizability ([13])	$-\Delta\chi \cdot 10^6 = -(-\chi_d - \chi_{\text{exp}}) \cdot 10^6$	$\chi_p \cdot 10^6$ from deformation	ΔE, eV	M_{01}, μ_B
AlAs	Al	5,661	18,8	47,4	–	–	–	–	–	2,2	–
AlAs	As	5,661	28,6	47,4	–	–	–	–	–	2,2	–
GaAs	Ga	5,654	26,4	51,2	32,4	47,6	70,5	18,8	37,6	1,4	0,185
GaAs	As	5,654	24,8	51,2	32,4	47,6	70,5	18,8	37,6	1,4	0,185
InAs	In	6,058	43,9	71,9	55,3	64,1	88,98	16,6	33,68	0,47	0,066
InAs	As	6,058	28,0	71,9	55,3	64,1	88,98	16,6	33,68	0,47	0,066
AlSb	Al	6,136	16,7	58,6	–	–	–	–	–	1,60	–
AlSb	Sb	6,136	41,9	58,6	–	–	–	–	–	1,60	–
GaSb	Ga	6,118	26,0	65,9	38,4	60,7	93,6	27,5	55,2	0,77	0,110
GaSb	Sb	6,118	39,9	65,9	38,4	60,7	93,6	27,5	55,2	0,77	0,110
InSb	In	6,475	40,2	80,1	65,9	77,2	114,28	14,2	48,38	0,26	0,047
InSb	Sb	6,475	39,9	80,1	65,9	77,2	114,28	14,2	48,38	0,26	0,047

The regularities in the variation of χ_d and χ_p as functions of the positions of the components in the periodic system of D. I. Mendeleev are noteworthy. In particular, it should be noted that the value of $\Delta\chi$ for gallium arsenide and antimonide is considerably larger than for the arsenides and antimonides of indium. The absolute values of M_{01} amount to tenths or hundredths of a Bohr magneton. Estimates of χ_p from the magnitude of the polarizability are apparently less reliable than those determined from X-ray data. The X-ray data obtained make it possible to solve the inverse problem and determine the magnitude of the polarizability of the compounds.

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Received
27 VII 1962

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