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Abstract

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THE PARAMAGNETIC COMPONENT OF THE MAGNETIC SUSCEPTIBILITY OF SEMICONDUCTING COMPOUNDS $A^{III}B^{V}$ FROM X-RAY DIFFRACTION ANALYSIS DATA

Until recently, the problem of separating the paramagnetic and diamagnetic components of the magnetic susceptibility of various substances remained unresolved; Ya. G. Dorfman paid special attention to the importance of this problem for clarifying questions of chemical bonding ([1,2]). The methods proposed in recent years for determining the dia- and paramagnetic components of magnetic susceptibility from X-ray diffraction analysis data ([3–5]) open up new possibilities and at the same time require further development.

Of particular interest is the determination, from X-ray diffraction analysis data, of the paramagnetic component of the magnetic susceptibility in semiconducting compounds $A^{III}B^{V}$. As is known, $A^{III}B^{V}$ compounds belong to the class of diamagnetics with a comparatively large paramagnetic component, determined as the difference between the magnetic susceptibility measured directly by experiment and the diamagnetic component, calculated theoretically ([1,6]) or determined by X-ray diffraction ([3,4]).

According to X-ray determinations of electron-density distributions ([7–12]), semiconducting compounds $A^{III}B^{V}$ with the sphalerite structure are characterized by the presence of clearly expressed covalent "bridges," which testify to the nature and peculiarities of the interatomic bond in these compounds. As was shown ([5]), the paramagnetic component of the magnetic susceptibility can be determined from experimental maps of the electron-density distribution. The present article presents a development of the experimental method for determining the paramagnetic component from X-ray diffraction analysis data, the form and degree of nonsphericity of the covalent "bridges" formed by sp^3-electrons, and gives the results of calculations of χ_p for arsenides and antimonides of aluminum, gallium, and indium.

The form of the covalent "bridge" in most cases can be approximated by a three-dimensional Gaussian function
$\rho = B\exp[-\gamma x^2 - \beta(y^2 + z^2)]$, with the origin at the center of the bridge and the

x-axis along the bond. Direct checking on maps in the plane perpendicular to the direction of the bond showed that the chosen function describes the character of the electron distribution in the bridge sufficiently well. The parameter β for each substance was determined directly from the experimentally determined map of the electron-density distribution.

The coefficient B is defined as a quantity equal to the electron density at the center of the "bridge" at $x = 0,\ y = 0,\ z = 0$. Since the covalent sp^3 bond is formed by a pair of electrons, the normalization condition

$$2 = \int_V \rho \, dV$$

determines the parameter γ. In this case

$$\gamma = B^2 \pi^3 / 4\beta^2.$$

The electron density ρ of the covalent bridge is equal to the square of the wave function of the electron cloud under consideration,

$$|\psi_0|^2 = \rho.$$

In this case the Van Vleck term, characterizing the paramagnetic component of the magnetic susceptibility ([1,5,13]), for four bonds is determined as

$$\chi_p = \frac{8}{3} \frac{N\mu_B^2}{\Delta E \hbar^2} \int \psi_0^* m^2 \psi_0 \, dV,$$

where m^2 is the operator of the square of the angular momentum; ΔE is the width of the forbidden band, μ_B is the Bohr magneton. Then

$$\chi_p = \frac{8N\mu_B^2}{3\frac{\beta}{\gamma}\Delta E} \left(\frac{\beta}{\gamma} - 1 \right)^2 = 86.1 \cdot 10^{-6} \frac{(\beta/\gamma - 1)^2}{\frac{\beta}{\gamma}\Delta E}.$$

In this formula ΔE is expressed in electron-volts.

Table 1

Quantities characterizing the distribution of sp^3-electrons of the bond

Compound	B, el/Å^3	γ, Å^{-3}	β, Å^{-2}
AlAs	0.40	0.71	1.32
GaAs	0.42	1.68	0.89
InAs	0.40	0.81	1.24

Compound	B, el/Å^3	γ, Å^{-3}	β, Å^{-2}
AlSb	0.38	0.66	1.28
GaSb	0.30	0.64	1.04
InSb	0.28	0.76	0.89

The values of B, γ, and β, determined from electron-density maps for the arsenides and antimonides of aluminum, gallium, and indium, are given in Table 1. This table, characterizing the shape of the covalent bridges, indicates, in particular, the existence of a certain anomaly in the position of the bridge in gallium arsenide.

Table 2 gives the results of calculating the paramagnetic component in the compounds $A^{\mathrm{III}}B^{\mathrm{V}}$ studied.

Consideration of the change in the quantity

$$\delta = \frac{(\beta/\gamma - 1)^2}{\beta/\gamma},$$

which characterizes deviations from sphericity of the sp^3-electron cloud of the bond, as a function of the position of the components in D. I. Mendeleev’ s periodic system, shows that the quantity δ, with increasing period number, decreases except for AlAs.

Table 2

X-ray-determined values of the para- and diamagnetic components of the magnetic susceptibility of the arsenides and antimonides of aluminum, gallium, and indium

Compound	Paramagnetic component, $\chi_p \cdot 10^6$	Diamagnetic component, $-\chi_d \cdot 10^6$ (4)	$-(\chi_p + \chi_d) \cdot 10^6$	Experimental value, $-\chi_{\mathrm{exp}} \cdot 10^6$ (6)	$\delta = \frac{(\beta/\gamma - 1)^2}{\beta/\gamma}$
AlAs	15.5	47.4	32.0	–	0.40
GaAs	24.6	51.2	26.6	32.4	0.41
InAs	25.8	71.9	46.1	55.3	0.14
AlSb	24.5	58.6	34.1	–	0.45
GaSb	26.4	65.9	39.5	38.4	0.24
InSb	8.1	80.1	72.0	65.9	0.03

The results of the present work indicate, first, that the developed X-ray method makes it possible to obtain comparatively reliable values of the magnetic susceptibility of semiconductor compounds with an accuracy comparable to that of experimental determinations, and, second, to carry out an independent determination of the dia- and paramagnetic components of the magnetic susceptibility.

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

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