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Abstract

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MAGNETIC SUSCEPTIBILITY OF SEMICONDUCTING ELEMENTS OF GROUP IV ACCORDING TO X-RAY DIFFRACTION ANALYSIS DATA

This paper presents the results of determining the dia- and paramagnetic components of the magnetic susceptibility of diamond, silicon, germanium, and gray tin from experimental X-ray diffraction data on the electron distribution in these elements.

The problem of separately determining the dia- and paramagnetic (Langevin χ_d and Van Vleck χ_p) components of magnetic susceptibility, the importance of which was emphasized by Ya. G. Dorfman ([1,2]), is at present of special interest as applied to semiconductors in which sp^3 bonding occurs. Determination of the components χ_d and χ_p from X-ray diffraction analysis data ([3–6]) under modern conditions is apparently the only method that makes it possible to carry out an independent determination of the indicated components of magnetic susceptibility.

In calculating the dia- and paramagnetic components for diamond, data on the electron-density distribution ([7]), obtained on the basis of the f-curve of Brill, Grimm, Hermann, and Peters ([8])*, were used; for silicon, germanium, and gray tin our experimental results ([9,10]) were used. The methods of calculation and the relations employed in this process are given in papers ([3–6]). From the data obtained by us, using Kirkwood' s formula ([1,11]), the values of the polarizability were also calculated in the present work.

Table 1

Diamagnetic components, polarizabilities, shortest interatomic distances, and covalent radii according to X-ray diffraction analysis data

Element	Shortest interatomic distance, Å	$-\chi_d \cdot 10^6$ by X-ray diffraction analysis	$-\chi_d \cdot 10^6$ ([2])	$-\chi_d \cdot 10^6$, theor. ([12])	Covalent radius according to X-ray diffraction data, r_d, Å	Covalent radius according to Pauling ([13]), Å	Polarizability α according to X-ray diffraction data	Polarizability ([2])
C (diamond)	1.44	7.2	7.4	6.8	0.79	0.77	0.9	0.96
Si	2.35	17.8	22.4	17	1.22	1.17	2.3	3.7
Ge	2.44	30.8	37	23.9	1.45	1.22	3.1	4.5
α-Sn	2.8	41.1	61	38.2	1.46	1.40	3.5	7.7

Table 1 gives the values of the shortest interatomic distances in the lattices of C (diamond), Si, Ge, and α-Sn, and the values of the diamagnetic susceptibility χ_d, polarizability α, and covalent radii calculated from the electron-density distribution data. For comparison, literature values are also given for the polarizability ([2]), the diamagnetic component determined from experimental values of the polarizability ([2]), theoretical values of χ_d according to the data of Busch and Kern ([12]), and covalent radii according to Pauling ([13]).

The X-ray diffraction values obtained for the diamagnetic component of magnetic susceptibility are in good agreement with the theoretical values obtained by Busch and Kern ([12]), and somewhat less well with the values calculated from the polarizability values ([2]).

* In calculating the magnetic susceptibility, the forbidden reflection (222) was taken into account.

The magnitude of the paramagnetic, or Van Vleck, component was determined from the shape and magnitude of the covalent "bridge" of the sp^3 bond. Assuming, as before ([5,6]), on the basis of an analysis of the experimental data, that the covalent "bridge" of the sp^3 bond is an electron cloud in the form of an ellipsoid of revolution, or a dumbbell, the electron-density distribution can be described by one or two three-dimensional Gaussian curves with the origin of coordinates at the center of the "bridge"

$$\rho = B_1 \exp\left[-\gamma_1\left(x - \frac{R}{2}\right)^2 - \beta_1(y^2 + z^2)\right] +$$

$$+B_2 \exp\left[-\gamma_2\left(x+\frac{R}{2}\right)^2-\beta_2(y^2+z^2)\right].$$

A practically sufficiently reliable description of the electron-density distribution of the sp^3 bond in the elements studied can be obtained by means of a single three-dimensional Gaussian curve

$$\rho = B\exp[-\gamma x^2-\beta(y^2+z^2)].$$

In that case

$$\chi_p = 86.1\cdot 10^{-6}\cdot\frac{(\beta/\gamma-1)^2}{\frac{\beta}{\gamma}\Delta E} = 86.1\cdot 10^{-6}\cdot\frac{\delta}{\Delta E}.$$

The magnitude B is determined from the height of the "bridge" at $x=0$, $y=0$, $z=0$; the magnitude β, experimentally, from the electron-density distribution map according to the steepness of the fall of electron density in the plane perpendicular to the direction of the sp^3 bond; and γ, from the normalization condition $\int \rho\, dV = 2$, corresponding to the number of electrons forming the bond.

Table 2

Quantities characterizing the dimensions and shape of the covalent "bridge" of the sp^3 bond

Element	Height of the "bridge" B, el/Å^3	β, Å^{-2}	γ, Å^{-2}	Nonsphericity, δ
C (diamond)	1.73	2.66	3.27	0.05
Si	0.49	1.51	0.81	0.39
Ge	0.54	1.06	2.00	0.42
α-Sn	0.32	1.00	0.79	0.06

The paramagnetic component is thus determined by the ratio of the measure of nonsphericity of the sp^3-electron cloud, δ, to the width of the forbidden band ΔE, eV.

Table 2 gives the values of B, γ, and β characterizing the shape of the covalent "bridge." These data indicate that in the series C–Si–Ge–α-Sn the electron density at the center of the "bridge" (the "height of the bridge") decreases, with the exception of Si–Ge. In Si the "height of the bridge" turns out to be somewhat smaller than in Ge. It should be noted that, considering the changes

in the quantities γ and β, one can arrive at the conclusion that the ellipsoidal cloud of the sp^3 bond in Si and α-Sn is elongated along the bond, while in C and Ge it is elongated across the bond. At the same time, the largest value of δ, characterizing the nonsphericity of the cloud, occurs for germanium, and the smallest for diamond and gray tin.

Table 3

Values of the paramagnetic component and the resulting magnetic susceptibility, determined radiographically, and experimental values

Element	$\chi_p \cdot 10^6$, radiogr.	$-\chi \cdot 10^6 = (\chi_p - \chi_d) \cdot 10^6$, radiogr.	$-\chi \cdot 10^6$, expt. ([12])	Width of the forbidden band ΔE, eV
C_2 (diamond)	0.7	13.7	11.8	5.5
Si_2	30.2	5.4	6.2	1.12
Ge_2	47.7	13.9	15.2	0.75
α-Sn_2	52.5	29.7	(63)	0.09

Table 3 gives the values, calculated from radiographic data, of the paramagnetic component and the total magnetic susceptibility, as well as experimental values of the magnetic susceptibility.

From Tables 1 and 3 it is evident that the diamagnetic and paramagnetic components are close in absolute magnitude and increase in the series C–Si–Ge–α-Sn, whereas the total value $-\chi$ passes through a minimum at Si. A comparison of the data in Tables 2 and 3 also shows that, owing to the small value of the asphericity and the large width of the forbidden band, diamond has a relatively small value of the paramagnetic component, while gray tin, although it has a small asphericity δ, has, because of the small magnitude of the forbidden band, a high value of the paramagnetic component.

A comparison of the resulting magnetic susceptibility, determined from X-ray diffraction data, with the experimental values of the susceptibility determined directly from magnetic measurements shows comparatively good agreement of these quantities for C, Si, and Ge. The reason for the discrepancy for gray tin requires further clarification.

The results of the investigation carried out also indicate that the determination of the magnetic susceptibility of semiconductors from X-ray diffraction data makes it possible to separate the dia- and paramagnetic components of the magnetic susceptibility, which so far is practically impossible to do by another method, and also to determine total values whose accuracy is comparable with that of values determined experimentally from magnetic-measurement data. The results obtained are undoubtedly of considerable interest.

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