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$$r_L = \left[\frac{1}{8} \sum_{\text{val}} \langle r^2 \rangle \right]^{1/2} = \left[\langle r^2 \rangle \sum_{\text{val}} \right]^{1/2}.$$

Theory of the Magnetic Susceptibility of Tetrahedral Semiconductors

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The magnetic susceptibility of an intrinsic tetrahedrally coordinated semiconductor is calculated using a tight-binding basis and approximations appropriate to the bond-orbital model. The susceptibility associated with the valence electrons is found to separate into a diamagnetic Langevin component and a paramagnetic Van Vleck component, both of which are found to be proportional to the square of the bond length, and nearly cancel in the homopolar semiconductors. The Langevin term is found to be approximately independent of polarity while the paramagnetic component varies with polarity, α_p , as $(1 - \alpha_p^2)^{3/2}$.

The measured magnetic susceptibility, χ , of a large class of semiconductors shows variations which seem to be related to the nature of the chemical bonding and in some cases to the presence or absence of long-range order.^{1,2} For example, the (diamagnetic) susceptibility of crystalline GaAs is about twice as large as that of crystalline Ge, and amorphous Ge is about 2.7 times more diamagnetic than crystalline Ge.¹

The purpose of this Letter is to present a simple model which elucidates the nature of the relationship between χ and the chemical bond for the class of tetrahedrally coordinated crystals.

It is relatively easy to evaluate the orbital magnetic susceptibility of a solid in terms of the exact eigenfunctions of the solid. This corresponds to treating the solid as a giant "molecule." However, as soon as one attempts to express the susceptibility in a tight-binding basis the necessity of maintaining gauge invariance presents complications. A general tight-binding theory considering these complications was presented earlier.³ The purpose of this Letter has been to evaluate the susceptibility obtained in Ref. 3 for

a model which both is simple and yet contains enough information to enable us to understand variations from material to material. For this purpose we chose the bond-orbital model.^{4,5} The advantage of this model lies in the fact that the coefficients of these hybrids involve parameters which have already been obtained for many semiconductors from dielectric and optical data. Furthermore, this model also allows a separate evaluation of the (valence electron) Langevin and Van Vleck contributions to χ . The calculation shows that whereas the main contribution to the Langevin-like terms χ_L is only weakly dependent on polarity, the paramagnetic contribution χ_p has a strong dependence. Our results indicate that the reduction of χ_p in the more polar crystals is caused not only by the larger gap between the valence and conduction states but also directly through a reduction of matrix elements in increasingly polar solids. This helps to explain the variation of the parameter B in the simple model for χ_p used by Hudgens, Kastner, and Fritzsche¹ to separate their measured susceptibilities into paramagnetic and diamagnetic com-

ponents.

In the bond-orbital model^{4,5} one starts with a set of four sp^3 hybrids on each atom in the system. As in the Weaire-Thorpe model⁶ only two types of interactions between the hybrids $h_{i\alpha}$ are included. These are a matrix element between two hybrids directed into a single bond, $-V_2$, and a matrix element between two hybrids on a single atom, $-V_1$. Empirically, it is found⁵ that V_2 is inversely proportional to the square of the bond length, i.e., $V_2 \propto d^{-2}$, a result we shall use later. The matrix element V_1 is related to the difference in energy of the atomic s and p states from which the hybrids are constructed by $V_1 = (\epsilon_p - \epsilon_s)/4$. For zinc blende crystals, with two different atoms in each primitive cell, there are two types of V_1 matrix elements which may be written $V_1^{(1)}$ and $V_1^{(2)}$. A third parameter V_3 defined as $V_3 = \frac{1}{2}[\langle h_c | H | h_c \rangle - \langle h_a | H | h_a \rangle]$, where the subscripts c and a stand for cation and anion, is also needed to describe heteropolar crystals.

One proceeds by making a unitary (actually an orthogonal) transformation to bond orbitals and antibonding orbitals,

$$|b, i\rangle = u_1 |h_{i1}\rangle + u_2 |h_{i2}\rangle, \quad (1)$$

$$|a, i\rangle = u_2 |h_{i1}\rangle - u_1 |h_{i2}\rangle, \quad (2)$$

with the parameters u_1 and u_2 to be determined through a minimization of the bond energy defined by $E_b = \langle b, i | H | b, i \rangle$. This minimization procedure yields the result $u_{1,2} = (1 \pm \alpha_p)^{1/2} / \sqrt{2}$, where the "polarity" parameter α_p is defined by $\alpha_p = V_3 / (V_2^2 + V_3^2)^{1/2}$. Notice that in the homopolar limit $V_3 = 0$ and $\alpha_p = 0$, while in the completely polar limit $V_2 = 0$ and $\alpha_p = 1$. Therefore α_p is very much like "ionicity" but is defined explicitly in terms of this approach. Similarly, the difference in the self-energy of the bonding and antibonding states is found to be $E_a - E_b = 2(V_2^2 + V_3^2)^{1/2}$ which is associated with^{4,5} the main optical-absorption peak. In deriving these results we have treated the hybrids centered on the various atomic sites as orthonormal.

One of us³ has derived an expression for the magnetic susceptibility of an intrinsic semiconductor that can be readily evaluated using the bond-orbital model (BOM). The susceptibility is decomposed into three terms:

$$\chi = \chi_c + \chi_L + \chi_p, \quad (3)$$

where

$$\chi_L = \frac{-e^2}{3mc^2\Omega} \sum_i \langle b, i | r_i^2 | b, i \rangle, \quad (4)$$

$$\chi_p = \frac{e^2}{m^2c^2\Omega(E_a - E_b)} \sum_{i,j} |\langle a, j | l_{zi} | b, i \rangle|^2, \quad (5)$$

and χ_c is the core-electron diamagnetic contribution. The indices i, j in Eqs. (4) and (5) label the bond sites; the coordinate $\vec{r}_i$ and the angular momentum l_{zi} are defined with respect to the local origin at the bond site i ; i.e., $r_i^2 = (x - X_i)^2 + (y - Y_i)^2 + (z - Z_i)^2$, where $\vec{R}_i = (X_i, Y_i, Z_i)$, is the position vector of the midpoint of the bond in question with respect to an arbitrary origin. The sum over spin variables has been made and contributed a factor of 2 in Eqs. (4) and (5). Ω is the volume of the crystal.

The transformation which defines the operators in Eqs. (4) and (5) with respect to the local bond origin generally leaves additional terms. The divergent terms proportional to R_i^2 arising from the diamagnetic and paramagnetic terms can be shown to cancel exactly^{3,7} for a general tight-binding Hamiltonian. The divergent terms proportional to $\vec{R}_i$ can also be shown to cancel. Thus, in this case, the susceptibility can be rigorously separated into two terms in analogy with a molecule.

The Langevin contribution, Eq. (4), corresponds to the second moment of the charge distribution of a bond in a plane normal to the direction of the applied field. The detailed evaluation of Eq. (4) is given elsewhere.⁷

It is found that the matrix element in Eq. (4) separates into a term proportional to d^2 and a second term proportional to $\alpha_p^2 M^2$, where M is an intra-atomic matrix element of the form $\langle s | x | p_x \rangle$. This matrix element is of the order of 0.7 Å which makes this term an order of magnitude smaller than that proportional to d^2 and makes the polarity dependence very weak. This suggests writing χ_L in the form

$$\chi_L = - (Ne^2/6mc^2)(\gamma_m d/2)^2 \quad (6)$$

where N is the electron density and γ_m is a scaling parameter of order unity which would equal 1 if the bond charge were concentrated at the atomic sites. It should be very nearly the same for all tetrahedrally bonded semiconductors. If we fit Eq. (6) to the experimental value for Si¹ we find $\gamma_m = 1.13$. Using this value of γ_m we list the values of χ_L obtained from Eq. (6) for a large number of crystals in Table I.

TABLE I. Bond-orbital-model parameters and the calculated values of the magnetic susceptibilities χ_L , χ_p , and χ . Experimental values are given in parentheses. The susceptibilities are in units of 10^{-6} cm³/mole.

COMPOUND	d (Å)	E _a -E _b (eV)	α_p	$-\chi_c^e$	$-\chi_L$	χ_p	$-\chi$
Si	2.35	4.4	0	~ 4.6	39.3	37.5	6.4(6.4) ^a
Ge	2.45	4.3	0	~ 14	42.7	38.5	18.2(15.7) ^a
α -Sn	2.80	3.52	0	32	55.8	48.4	39.4(63) ^a
GaP	2.36	5.10	0.52	9	39.6	23.7	24.9(30) ^a
GaAs	2.45	4.94	0.5	14	42.7	25.1	31.6(33.3) ^a
GaSb	2.65	4.32	0.44	22	50	30.9	41.1(38.4) ^b
InP	2.54	4.84	0.58	20	45.9	22.7	43.2(45.6) ^b
InAs	2.61	4.6	0.53	25	48.5	25.9	47.6(55.3) ^b
InSb	2.81	4.08	0.51	33	56.2	30.1	59.1(65.9) ^b
ZnS	2.34	6.36	0.73	11	39	12.1	37.8(39.5) ^b
ZnSe	2.45	6.24	0.72	15	42.7	14.6	43.1(46.5) ^b
CdS	2.53	6.16	0.77	23	45.6	10.9	57.7(53.3) ^b
CdSe	2.63	6.10	0.77	27	49.2	11.0	65.2(63.9) ^b
CdTe	2.81	5.44	0.76	34	56.2	12.9	78.0(84) ^b
HgS	2.53	6.66	0.75	38	44.1	10.9	71.3 ^d (55.4) ^c
HgSe	2.64	6.36	0.77	42	49.6	10.6	81. (58.7)
HgTe	2.76	5.70	0.76	49	54.2	12.2	91.0(75.8)
CuCl	2.34	6.58	0.75	12	39.0	11.0	40(46) ^b
CuBr	2.49	7.02	0.79	~ 14	44.1	8.8	52.5(56.2) ^b
AgI	2.80	6.36	0.83	34	55.8	8.1	90.5(90.6) ^b
C	1.55	12.2	0	0.2	17.1	4.4	12.9(11.8) ^{a,b}
BN	1.57	13.4	0.41	0.3	17.5	4.0	13.8
BeO	1.65	15.86	0.64	0.4	19.4	3.4	16.4(11.93) ^c

^aRef. 1.^bRef. 9.^cRef. 10.^dZinc-blende structure.^eRef. 11.

An important point first recognized by Van Vleck⁸ in the case of molecules and emphasized by White³ for crystals is that any separation of the valence-electron diamagnetic (χ_L) and paramagnetic (χ_p) contributions to the susceptibility is not unique but depends upon the choice of origin. In obtaining Eq. (6) for χ_L we have used a local origin at a bond center and we will use the same local origin in evaluating the paramagnetic susceptibility χ_p . The relatively good agreement between our calculated values of χ_L (with the origin at a bond site) with the experimentally determined values of Ref. 1 therefore seems to suggest that the authors of Ref. 1 have implicitly chosen a bond-site origin in decoupling the diamagnetic and paramagnetic contributions to the susceptibility.

Let us now consider the Van Vleck contribution

to the magnetic susceptibility, given by Eq. (5). Because of the cylindrical symmetry of the bonds the angular momentum operator has no intra-bond matrix elements. We must therefore evaluate the matrix elements between a bonding orbital at site i with a nearest-neighbor antibonding orbital at $i + \delta$. For example, considering the matrix element $\langle a, i + \delta | l_{zi} | b, i \rangle$, where the subscript i on l_{zi} denotes that the origin is at the bond site i . To evaluate this we translate the origin from site i to the joint atomic site. This can be done by using the relation

$$l_{zi} = l_{z2} + (\vec{\delta}_{2i} \times \vec{p})_z. \quad (7)$$

Then

$$\langle a, i + \delta | l_{zi} | b, i \rangle = L_1 + L_2, \quad (8)$$

where L_1 and L_2 follow from Eq. (7).

The matrix element L_1 in Eq. (8) can be easily evaluated by expanding the orbitals in sp^3 hybrids. There are intra-atomic terms which we expect to be dominant. Let us define the unit vectors $\vec{\tau}_1 = (1, 1, 1)/\sqrt{3}$, $\vec{\tau}_2 = (1, \bar{1}, \bar{1})/\sqrt{3}$, $\vec{\tau}_3 = (\bar{1}, 1, \bar{1})/\sqrt{3}$, and $\vec{\tau}_4 = (\bar{1}, \bar{1}, 1)/\sqrt{3}$ which are directed from a site to the four nearest-neighbor atoms. We then find

$$L_1 = \pm \frac{3\hbar}{i} \frac{u_1 u_2}{4} (\vec{\tau}_i \times \vec{\tau}_{i+\delta})_z \quad (9)$$

where the plus (minus) sign is to be taken when the common origin is at an anion (cation) site. The product $u_1 u_2$ is equal to $\frac{1}{2}(1 - \alpha_p^2)^{1/2}$ thus making L_1 a decreasing function of polarity. When the matrix element L_2 is expressed in terms of the unit basis it becomes

$$L_2 = \frac{1}{8}(\sqrt{3}d)u_1 u_2 \langle s|p_x|x\rangle (\vec{\tau}_i \times \vec{\tau}_{i+\delta})_z. \quad (10)$$

We have used the relations $\langle s|p_y|y\rangle = \langle s|p_x|z\rangle = \langle s|p_x|x\rangle$. By writing $\vec{p} = m[\vec{r}, \mathcal{H}]/i\hbar$ we may convert this to a matrix element of the coordinate r_i and finally write the result in terms of a dimensionless oscillator strength f_{sp} for the s - p transition in the atom. Adding the result to Eq. (10), squaring, and carrying out the sums indicated in Eq. (5) we obtain the paramagnetic contribution

$$\chi_p = \frac{Ne^2 \hbar^2 \lambda^2 (1 - \alpha_p^2)}{8m^2 c^2 (E_a - E_b)}, \quad (11)$$

where again N is the electron density and $\lambda = 1 - (mV_1 d^2 f_{sp} / 6\hbar^2)^{1/2}$. This result naturally reveals the polarity or ionicity dependence associated with the parameter B in the work of Hudgens, Kastner, and Fritzsche.¹ It is observed that f_{sp} and V_1 do not vary appreciably from atom to atom. Therefore we expect λ to remain nearly constant for all compounds. In fact, λ varies from 0.52 for tin to 0.71 for diamond. Because of the limitations associated with the bond-orbital model as discussed elsewhere,⁷ we do not expect this model to give a quantitative estimate for λ . We have therefore determined λ by fitting Eq. (11) to the experimental value¹ of χ_p for Si. This gives $\lambda = 1.13$, which when used for other semiconductors gives reasonable values as shown in Table I and Fig. 1.

The first row semiconductors C, BN, and BeO are exceptions in the sense that $V_1 \ll V_2$. In this case matrix elements of $\vec{p}$ between hybrids on different centers become important. In this limit the value of λ becomes $1 - (mV_2^2 d^2 f_{sp} / 24\hbar^2 V_1)^{1/2}$.

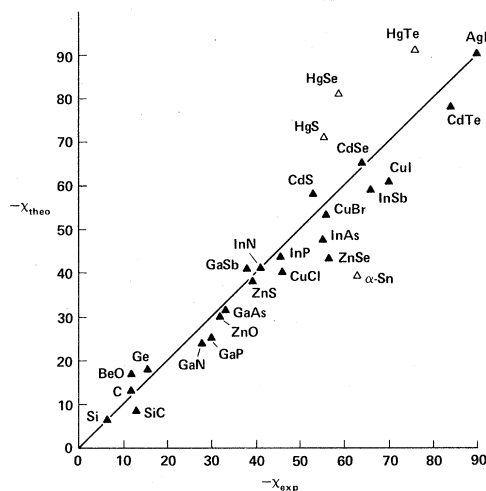


FIG. 1. Comparison between the bond-orbital-model predictions for the total susceptibility and the experimental values. The open triangles are semimetals while the others are semiconductors. The straight line has slope unity. The parameters γ_m in Eq. (6) and λ in Eq. (11) were determined by fitting the experimental data for Si.

Using this result we obtain the values for the susceptibilities also shown in Table I. We see in this case the bond-orbital model works very well.

From Fig. 1 we see that the compounds which deviate most from this theory are the semimetals. It also appears that the theoretical values are smaller in magnitude than the experimental values.

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