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Magnetic susceptibility of InP, InAs, and InSb

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The diamagnetic susceptibility χ of InP, InAs, and InSb is calculated with use of a linear combination of hybrid orbitals model recently developed by us. Our expression for χ, which is derived from the general expression for the diamagnetic susceptibility of intrinsic semiconductors, is independent of the choice of origin and free from any scaling parameter, unlike as in the earlier theory.

There have been extensive theoretical and experimental investigations of the physical properties of InB^{V} compounds[1] (InP, InAs, and InSb) because of their importance in science and technology. In recent years, the development of low-dimensional semiconductor structures, which are potentially of great importance for many high-speed electronic and optoelectronic devices, has further increased interest in the study of these materials. Several attempts have been made to understand the electronic, optical, and magnetic properties of these solids. Hudgens, Kastner, and Fritzsche[2] first showed that the magnetic susceptibility (χ) of $A^N B^{8-N}$ semiconductors can be described by a simple chemical-bond model. Chadi, White, and Harrison[3] (CWH) have used a tight-binding basis[4] and approximations appropriate to the bond orbital model[5,6] to obtain an expression for χ of $A^N B^{8-N}$ semiconductors. However, in the CWH theory, arbitrary scale factors have been used to fit with the experimental results. Further, the complete problem of the magnetic susceptibility of solids[7–9] has not been considered in their theory. In fact, experiments[10] on the temperature dependence of χ of $A^N B^{8-N}$ semiconductors indicate that there are substantial deficiencies in their theory.

Recently we have formulated a theory[11,12] to calculate the magnetic susceptibility of tetrahedral semiconductors by introducing a linear combination of hybrid orbitals model. We have constructed a basis set for the valence bands which is a linear combination of sp^3 hybrid orbitals forming a bond in which their relative phase factors, heretofore neglected, have been properly included. We have also constructed a basis set for the conduction bands which are orthogonal to the valence-band functions. We have constructed localized Wannier functions[13] from our Bloch functions and have shown that the bond orbitals used in the earlier theories[3,4] are not a proper choice for the Wannier functions of the valence band. We have derived a general expression for χ of intrinsic semiconductors by using a finite-temperature Green's-function formalism. We have shown that terms of same order have been missed in the earlier theories[3,4,14] of χ. We have used our basis states in our general expression for χ and calculated χ of tetrahedral semiconductors.[12,15] Our results have agreed well with the experiment.[2] We note that our expression for χ is origin independent and free from any scaling parameter. It is interesting to note that our formalism for χ of elemental semiconductors[11] has been used[16] to explain the anomalous diamagnetic susceptibility of amorphous Si and Ge. It is further interesting to note that our results of χ of AlAs have been used[17] as a basic material parameter to estimate the magnetic susceptibility of the alloy compound $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$.

In the present paper we use our formalism to calculate the magnetic susceptibility of InB^{V} compounds. We consider a zinc-blende structure where each In atom is surrounded tetrahedrally by four group-V atoms B^{V} (say, P, As, or Sb). Similarly each group-V atom B^{V} is surrounded tetrahedrally by four In atoms. The standard primitive cell contains two basis atoms at site i, with four sp^3 hybrid orbitals $h_j^V(\mathbf{r}-\mathbf{R}_i)$ pointing from group-V atom B^{V} (say, group-V atom) to the nearest-neighbor In atom along the directions j ($j=1,\ldots,4$) and four other sp^3 hybrid orbitals $h_j^{\mathrm{In}}(\mathbf{r}-\mathbf{R}_i-\mathbf{d}_j)$ pointing from these nearest neighbors to group-V atom B^{V}. We choose one of the group-V atomic sites as the origin. $\mathbf{R}_i$ is a lattice vector for site i and $\mathbf{d}_j$ is a nearest-neighbor vector. We construct Bloch-like tight-binding sums for the valence-band basis functions by taking linear combination of hybrid orbitals forming a bond

$$O_j^v(\mathbf{r},\mathbf{k})=\frac{1}{\sqrt{N}}\sum_i C_j^v(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{R}_i)O_{i,j}^v(\mathbf{r},\mathbf{k}) , \tag{1}$$

where

$$C_j^v(\mathbf{k})=[1+\lambda^2+2\lambda S\cos(\mathbf{k}\cdot\mathbf{d}_j)]^{-1/2} , \tag{2a}$$

$$O_{i,j}^v(\mathbf{r},\mathbf{k})=h_j^V(\mathbf{r}-\mathbf{R}_i)+\lambda h_j^{\mathrm{In}}(\mathbf{r}-\mathbf{R}_i-\mathbf{d}_j)\exp(i\mathbf{k}\cdot\mathbf{d}_j) . \tag{2b}$$

S is the overlap integral and λ accounts for the partial ionic character of the compounds via Coulson's ionicity parameter $f_C=(1-S^2)^{1/2}(1-\lambda^2)/(1+\lambda^2+2\lambda S)$. The basis functions for the conduction bands are obtained by constructing functions orthogonal to $O_j^v(\mathbf{r},\mathbf{k})$:

$$O_j^c(\mathbf{r},\mathbf{k})=\frac{1}{\sqrt{N}}\sum_i C_j^c(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{R}_i)O_{i,j}^c(\mathbf{r},\mathbf{k}) , \tag{3}$$

where

$$C_j^c(\mathbf{k})=\left[\frac{\lambda+S\exp(-i\mathbf{k}\cdot\mathbf{d}_j)}{(1-S^2)(1+\lambda^2+2\lambda S\cos\mathbf{k}\cdot\mathbf{d}_j)[\lambda+S\exp(i\mathbf{k}\cdot\mathbf{d}_j)]}\right]^{1/2} \tag{4}$$

and

$$O_{i,j}^c(\mathbf{r},\mathbf{k})=[\lambda+S\exp(i\mathbf{k}\cdot\mathbf{d}_j)]h_j^V(\mathbf{r}-\mathbf{R}_i)-[\lambda S+\exp(i\mathbf{k}\cdot\mathbf{d}_j)]h_j^{\mathrm{In}}(\mathbf{r}-\mathbf{R}_i-\mathbf{d}_j)\ . \tag{5}$$

We construct the Bloch eigenfunctions for the valence (n) and conduction (m) bands as

$$\Psi_n(\mathbf{r},\mathbf{k})=\sum_j \alpha_{jn}^v(\mathbf{k})O_j^v(\mathbf{r},\mathbf{k})\ , \tag{6}$$

$$\Psi_m(\mathbf{r},\mathbf{k})=\sum_j \alpha_{jm}^c(\mathbf{k})O_j^c(\mathbf{r},\mathbf{k})\ . \tag{7}$$

α's are elements of 4×4 matrices which satisfy the unitary properties $\sum_n \alpha_{jn}^v(\mathbf{k})\alpha_{nj'}^{v+}(\mathbf{k})=\delta_{jj'}$ and $\sum_m \alpha_{jm}^c(\mathbf{k})\alpha_{mj'}^{c+}(\mathbf{k})=\delta_{jj'}$. We use the Bloch functions [Eqs. (6) and (7)] to evaluate the matrix elements in the expression for χ of intrinsic semiconductors recently derived by us,[12] which can be written as

$$\begin{aligned}\chi=(2h_{\alpha\beta}h_{\gamma\delta}/B^2)\sum_{n,\mathbf{k}}[&-(\hbar^2/m)Q_{nm}^{+\alpha}Q_{mn}^{\gamma}\delta_{\delta B}+Q_{nm}^{+\alpha}Q_{mn'}^{\gamma}P_{n'm'}^{\delta}Q_{m'n}^{\beta}+P_{nm}^{\alpha}Q_{nm'}^{\gamma}Q_{n'm'}^{+\beta}Q_{m'n}^{\delta}-Q_{nm}^{+\alpha}P_{mn'}^{\gamma}Q_{n'm'}^{+\beta}Q_{m'n}^{\delta}\\&+2Q_{nm}^{+\alpha}Q_{mn}^{\beta}P_{nm'}^{\gamma}Q_{m'n}^{\delta}+2P_{nn'}^{\alpha}Q_{n'm}^{+\beta}P_{mm'}^{\gamma}Q_{m'n}^{\delta}/E_{m'n'}-Q_{nm}^{+\alpha}P_{mm'}^{\beta}P_{m'm''}^{\gamma}Q_{m''n}^{\delta}/E_{m'n}\\&+P_{nn'}^{\alpha}Q_{n'm}^{+\beta}P_{mm'}^{\gamma}Q_{m'n}^{\delta}/E_{mn}]=\chi_1+\chi_2+\cdots+\chi_8\ .\end{aligned} \tag{8}$$

Here

$$Q_{mn}^{\alpha}=-\int U_m^*\nabla_{\mathbf{k}}^{\alpha}U_n d\mathbf{r},\quad h_{\alpha\beta}=\epsilon_{\alpha\beta\gamma}h^{\gamma},\quad \mathbf{h}=e\mathbf{B}/2\hbar c,\quad E_{mn}=E_{m\mathbf{k}}-E_{n\mathbf{k}}\ ,$$

and $P_{nm}/\hbar$ are the matrix elements of the velocity operator between Ψ_n and Ψ_m. U_n and U_m are periodic parts of the Bloch function, $(n,n',\ldots)$ and $(m,m',\ldots)$ denote the valence and conduction bands, and repeated indices imply summation. We have used the completeness relation to express the matrix elements in terms of valence-band functions and the Hall-Weaire-Thorpe approximation[18,19] to calculate the matrix elements between different hybrids. Furthermore, we make an average-energy-gap ansatz and obtain

$$\chi_1+\chi_2+\chi_5=\chi_v^1+\chi_v^2\ , \tag{9}$$

where

$$\chi_v^1=-\frac{4e^2}{mc^2}[A_j(\langle x^2\rangle_V+\lambda^2\langle x^2\rangle_{\mathrm{In}})+2\lambda A_{2j}\langle x(x-d_j^x)\rangle_{12}]\ , \tag{10}$$

$$\begin{aligned}\chi_v^2=-\frac{4e^2}{mc^2}\{&\lambda[-\lambda A_{3j}+A_{4j}(\langle x^2-xy\rangle_V+\lambda^2\langle x^2-xy\rangle_{\mathrm{In}}+2\lambda A_{5j}\langle x(x-d_j^x-y+d_j^y)\rangle_{12}]\\&+[A_{6j}(M_V-\lambda^2M_{\mathrm{In}})+A_{7j}(P_V-\lambda^2P_{\mathrm{In}})]\}\ .\end{aligned} \tag{11}$$

Further,

$$\chi_3+\chi_4=0,\quad \chi_6+\chi_7+\chi_8=\chi_p^1+\chi_p^2\ , \tag{12}$$

where

$$\chi_p^1=\frac{2e^2\hbar^2S^2}{m^2c^2E_g(1-S^2)}[(1+\lambda^2)^2B_{ljj'}-4\lambda^2B_{2jj'}]\ , \tag{13}$$

$$\begin{aligned}\chi_p^2=\frac{2e^2\hbar^2S}{m^2c^2E_g(1-S^2)}\{&B_{3jj'}+[B_{4jj'}(2\langle x\rangle_{12}-Sd/\sqrt{3})+B_{5jj'}(1-\lambda^2)-B_{6jj'}(M_V-M_{\mathrm{In}})\\&+B_{7jj'}(M_V-\lambda^2M_{\mathrm{In}})+B_{8jj'}(P_V-\lambda^2P_{\mathrm{In}})]\}\ .\end{aligned} \tag{14}$$

Here j is chosen in the (111) direction, $j'\neq j$, $\langle\theta\rangle=\langle h_j^{\alpha}|\theta|h_j^{\alpha}\rangle$ $(\alpha=V,\mathrm{In})$, $\langle\theta\rangle_{12}=\langle h_j^V(\mathbf{r})|\theta|h_j^{\mathrm{In}}(\mathbf{r}-\mathbf{d}_j)\rangle$, $M_{\alpha}=\langle s_{\alpha}|x|p_{x\alpha}\rangle$, $P_{\alpha}=\langle s_{\alpha}|d/dx|p_{x\alpha}\rangle$ and $A_{1j},A_{2j},\ldots$ and $B_{ljj'},B_{2jj'},\ldots$ are functions of the above parameters involving summation over $\mathbf{k}$. s_{α} and $p_{x\alpha}$ are atomic orbitals and E_g is the average energy gap. We note that χ_v^1 and χ_p^1 are the results which can be obtained by using our basis functions in the Langevin and Van Vleck terms of White.[4] χ_v^2 and χ_p^2 are additional terms of equal order obtained by us. In order to compare

TABLE I. Diamagnetic susceptibility of InB^{V} compounds (χ in 10^{-6} cm^3/mole).

Solid	d (A)	S	λ[a]	E_g[a] (eV)	χ_c[b]	χ_v^1	χ_v^2	χ_p^1	χ_p^2	χ	χ_{expt}[c]
InP	2.54	0.598	0.221	4.84	−20.0	−35.4	−15.5	22.6	6.6	−41.7	−45.6
InAs	2.61	0.611	0.263	4.6	−25.0	−40.2	−14.7	24.1	10.0	−45.8	−55.3
InSb	2.81	0.633	0.267	4.08	−33.0	−51.5	−19.8	30.2	11.6	−62.5	−65.9

[a] Reference 6.
[b] Reference 23.
[c] Reference 22.

our results with that of CWH, we note that if we consider the extreme tight-binding case, our expression for χ_v^1 reduces to the expression for χ_L of CWH [Ref. 3 and Eq. (4)]. However, there is a significant difference between our expression for χ_p and that of the earlier theory. We note that our expressions for χ_v^2, χ_v^2, χ_p^1, and χ_p^2 are independent of the choice of origin and free from any scaling parameter, whereas in the earlier theory arbitrary scaling parameters have been used to obtain their results which compensates for the terms missed by them as well as the deficiencies in their model.

We have calculated χ of InP, InAs and InSb using Hartree-Fock orbitals from Clementi and Roetti's table.[20] We have used a spheroidal transformation technique[21] to calculate the two-centered integrals. The coefficients $A_{1j}, A_{2j}, \ldots$ and $B_{1jj'}, B_{2jj'}, \ldots$ are evaluated by carrying out the **k** integration over a sphere of volume equal to that of the Brillouin zone. In Table I, we present the values of d, λ, E_g, S, and the core diamagnetic susceptibility, χ_c, together with the results of various components of χ of InP, InAs, and InSb and the experimental results.[22] There is good agreement between our results and the experiment. We note that ionicity (λ) plays an important role in the results of various components of χ [Eqs. (11)–(15)]. Due to specific dependence of λ on different terms, we note that the dominant contribution to χ_v^1 is yielded from the anionic term. In χ_v^2, the first group of terms is proportional to λ. In the homopolar limit ($\lambda = 1$), the first term of the first group predominates over the other two terms and the second group of terms vanishes. Therefore χ_v^2, which is diamagnetic for ionic compounds, is weakly paramagnetic for group-IV semiconductors.[11] Further, we note that χ_p^1 and χ_p^2, which are proportional to $S^2/(1-S^2)E_g$ and $S/(1-S^2)E_g$, respectively, depend essentially upon the values of S, E_g, and λ. The small discrepancy between our results and experimental results can be accounted for due to the fact that we have not considered the mixing of bonding and antibonding states in the construction of the valence-band states. Further, our computation of χ is based on the Hall-Weaire-Thorpe approximation. Our results, in principle, can be improved by adopting a more realistic model, i.e., by including matrix elements between hybrid orbitals on adjacent atoms not forming a bond and also including matrix elements between hybrid orbitals on distant neighbors. Finally we note that we have used the values of core diamagnetic susceptibility (χ_c) from Ref. 23 which have been empirically obtained by Selwood. Since recent calculation[10] of χ_c of some other compounds yields more negative values than that of Selwood, we believe that our results would also be improved by using accurate values of χ_c. In conclusion, we note that, for the first time, we have calculated the magnetic susceptibility of InB^{V} compounds (InP, InAs, and InSb) by using an expression for χ which is derived from a general expression for χ of intrinsic semiconductors without using any scaling parameter. We believe that our formalism can also be applicable to nontetrahedral materials (such as Se and Te) with suitable modifications.

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[1] There are several books, monographs, and review articles dealing with the electronic structure and properties of InB^{V} compounds. Some of the examples are the series *Semiconductors and Semimetals,* edited by R. Willardson and A. Beer (Academic, New York); Marvin L. Cohen and J. R. Chelikowsky, *Electronic Structure and Optical Properties of Semiconductors* (Springer-Verlag, Berlin, 1988).

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