length of the test in which the dislocation traversed a distance of 40 lattice parameters. The computer simulation determination of $x(t)$ cannot be distinguished, on that scale, from that shown in Fig. 2. In another computer simulation of the model, the dislocation was first brought to steady conditions under an applied stress with $v=0.660$, and the stress then gradually reduced. At the time the stress reached zero, the measured dislocation velocity was $v=0.275$. After that time, it decreased very slowly so that after traversal of 65 lattice parameters under zero stress, at which time the computer simulation was terminated, the dislocation velocity had declined only to $v=0.264$. The velocity trend appeared to be approaching $v=0.25$ asymptotically. We conclude, therefore, that the loss-free mode can be attained in a natural manner.

It should be noted that the Peierls stress, σ_P, for this model, and the values of the model parameters here assumed, does not vanish. Rather, for $P=0.25$ and $\gamma=0.35$, the general theory[6,7] gives $\sigma_P=0.0506\mu$, where μ is the shear modulus of the crystal. Therefore, contrary to the frequent assumption,[10] the fact that the dislocation is subject to a periodic Peierls potential in its steady motion does not inevitably give rise to radiation losses, at least for the modified Frenkel-Kontorova model studied here. Whether such loss-free motion is possible in other models is a subject for further investigation, but in any case the present work demonstrates that the relationship between radiation losses and the periodic Peierls potential is not straightforward. The dynamic Peierls stress,[1] σ_{P_D}, for these parameters also has a nonzero value, namely $\sigma_{P_D}=0.7520\times10^{-3}\mu$. Therefore the result previously stated,[1] based on the local-mode approximation, that steady dislocation motion is possible only for $\sigma>\sigma_{P_D}$ is incorrect for the case when one starts with steady motion at $\sigma>\sigma_{P_D}$ and then slowly reduces the stress level. On the other hand, for the case of a dislocation starting from rest in an unstable configuration under an applied stress σ, it is necessary for $\sigma\gtrsim\sigma_{P_D}$ for continued motion to occur.[9]

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Diamagnetic Susceptibility of Tetrahedral Semiconductors*

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The lattice contribution to the diamagnetic susceptibility, χ_L, is written as a sum of three terms, a core term χ_c, a Langevin-like valence-electron contribution χ_v, and a Van Vleck paramagnetic term χ_p using a one-oscillator model. Measurements of χ_L and $d\chi_L/dT$ for diamond, Si, Ge, GaAs, and GaP are presented. The model allows a separate determination of each of the three terms and relates these terms to the symmetry and extent of the valence-bond charge distribution.

The purpose of this Letter is to show that chemical bonding and the diamagnetism of semiconductors are related in a simple way. A model is presented which describes the diamagnetism in terms of three contributions: two Langevin-like diamagnetic terms χ_c and χ_v which arise from the core and valence electrons, respectively, and a Van Vleck paramagnetic susceptibility χ_p which results from virtual magnetic dipole transitions between the valence and conduction bands.

With the values and the temperature dependencies of the magnetic susceptibility and the dielectric constant, this model makes it possible to determine χ_v and χ_p separately. We present measurements and analyses of the lattice contribution to the susceptibility, χ_L, of diamond, Si, Ge, GaAs, and GaP. Other contributions such as those from impurities and carriers are negligible in the temperature range chosen. Although theoretical expressions for the remaining lattice susceptibility χ_L have been derived[1,2] they are difficult to evaluate for real solids.

Magnetic susceptibility has been used for a long time as a probe of the details of chemical bonding in molecules.[3] Van Vleck[4] has shown for molecules that the molar susceptibility can be written as

$$\chi = -\frac{N_0 e^2}{6mc^2}\sum_{\text{core}}\langle r^2\rangle - \frac{N_0 e^2}{6mc^2}\sum_{\text{valence}}\langle r^2\rangle + 2N_0\sum_{i\neq j}\frac{|\langle i|\mu_\parallel|j\rangle|^2}{E_i - E_j}. \tag{1}$$

The first and second terms are the Langevin terms χ_c and χ_v, respectively. The third term is the Van Vleck paramagnetic susceptibility χ_p arising from virtual magnetic dipole transitions between filled and empty energy levels. Here r is the electron position vector, $\mu_\parallel$ is the component of the magnetic dipole operator in the field direction, and N_0 is Avogadro's number.

We expect that in a semiconductor χ_L is a sum of core and bond susceptibilities which can be described by Eq. (1). We approximate the Van Vleck term by a one-oscillator model with oscillator energy E_m. This energy is the average energy separation of valence- and conduction-band states connected by the magnetic dipole operator. Such an approximation is made by Phillips[5] to describe the dielectric susceptibility. He uses the Penn isotropic two-band model which gives the low-frequency dielectric constant approximately as

$$\epsilon(0) - 1 = (\hbar\omega_p/E_g)^2, \tag{2}$$

where E_g represents a weighted energy separation of valence- and conduction-band states connected by the electric dipole operator and $\hbar\omega_p$ is the valence-electron plasma energy.

In general E_g and E_m should be different. However, as long as the magnetic and electric dipole matrix elements vary slowly with energy, E_g and E_m will be proportional, $E_m = \beta E_g$ with β of order unity. In accordance with Eq. (1) we then write for semiconductors

$$\chi_L = -(N_0 e^2/6mc^2)\sum_{\text{core}}\langle r^2\rangle - (8N_0 e^2/6mc^2)\langle r^2\rangle_{\text{valence}} + B/\beta E_g. \tag{3}$$

Considering tetrahedral semiconductors in the following we have written χ_L for two atoms per unit cell, i.e. eight valence electrons. It should be emphasized that although χ_v is of the same form as χ_c, it arises from charge distributed over distances of covalent bond lengths or larger.[6]

B is proportional to an average interband magnetic dipole matrix element. It is sensitive to the symmetry of the chemical bonding. It is zero for spherically or cylindrically symmetric electron distributions for which $\mu_\parallel = \mu_B L_z$ is diagonal. This explains why χ_p is negligible for ionic materials in which the ions are approximately spherical. We expect B to be nearly the same for tetrahedral semiconductors which have the same bond symmetry because of the following argument.[7]

Consider the commutator

$$[[H, L_z], L_z] = HL_z^2 - 2L_zHL_z + L_z^2H.$$

When one takes the expectation of this for the

TABLE I. Measured values.[a]

	χ_L (10^{-6} cm^3/mole)	$d\chi_L/dT$ (10^{-9} cm^3/mole K)
C	-11.8 ± 0.2	-0.014 ± 0.006
Si	-6.4 ± 0.2	1.5 ± 0.06
Ge	-15.7 ± 0.5	3.6 ± 0.1
GaAs	-33.3 ± 1.0	1.2 ± 0.05
GaP	-30.0 ± 1.0	0.9 ± 0.04

[a] Most of these quantities have also been measured previously by G. A. Busch and R. Kern, Helv. Phys. Acta 32, 25 (1959); D. K. Stevens, J. W. Clelland, J. H. Crawford, Jr., and H. C. Schweinler, Phys. Rev. 100, 1084 (1955); and E. Sonder and D. K. Stevens, Phys. Rev. 110, 1027 (1958). The data presented here are somewhat more accurate and agree with the previous studies except for the values of χ_L of GaP and $d\chi/dT$ of GaAs.

TABLE II. Separated components of molar magnetic susceptibility.

	χ_c (10^{-6} cm^3/mole)	χ_v (10^{-6} cm^3/mole)	χ_p (10^{-6} cm^3/mole)
C	-0.3	-24.7 ± 4	13.2 ± 4
Si	-4.6	-39.3 ± 6	37.5 ± 6
Ge	-16.6	-50.3 ± 4	51.2 ± 4
GaAs	-16.6	-47.4 ± 3	30.7 ± 2
GaP	-11.7	-46.4 ± 3	28.1 ± 2

ground state $|s\rangle$, one obtains

$$\langle s|[[H, L_z], L_z]|s\rangle = -2\sum_n (E_n - E_s)\,|\langle s|L_z|n\rangle|^2,$$

where $|n\rangle$ is an excited state. Evaluating the left-hand side, where

$$H = P^2/2m + V(r), \quad L_z = (\hbar/i)\,\partial/\partial\varphi,$$

one obtains

$$\langle s|\hbar^2\,\partial^2 V/\partial\varphi^2|s\rangle = 2\sum_n (E_n - E_s)\,|\langle s|L_z|n\rangle|^2,$$

where φ is the azimuthal angle. Setting $E_n - E_s \approx \beta E_g$ as in Eq. (3) and using $\mu_{\parallel} = \mu_B L_z/\hbar$, we find that

$$B \approx (N_0 \mu_B^2/\beta E_g)\langle s|\partial^2 V/\partial\varphi^2|s\rangle. \tag{4}$$

Because E_g scales with V, i.e. the bond strength, B depends only on the symmetry of the potential or charge density.[8]

The terms χ_v and χ_p therefore contain information about the spatial extent and the symmetry of the bond charge. Earlier attempts[9] to effect this separation were not very successful. The temperature dependence of χ_L, however, can be used together with Eq. (3) and the calculated values for χ_c to determine χ_v and χ_p separately. We assume that $\langle r^2\rangle$ of the valence electrons has the same temperature coefficient as the square of the covalent bond length. This is reasonable for tetrahedral semiconductors but not for materials having a coordination smaller than four. The temperature dependence of χ_L is then given by[10]

$$d\chi_L/dT = 2\alpha\chi_v - \chi_p\, d\ln E_g/dT, \tag{5}$$

where α is the linear expansion coefficient and $\chi_p = B/\beta E_g$. The temperature dependence of the Penn-Phillips gap E_g is obtained from measurements of $d\epsilon(0)/dT$.

To test the model, measurements of the magnetic susceptibility and its temperature dependence were performed on high-purity single-crystal samples of diamond, Si, Ge, GaAs, and GaP by using the Faraday technique. For the diamond measurement the sample was composed of seven, $\frac{1}{3}$-carat gem-quality diamonds[11] which were determined by EPR to contain less than 1 part in 10^7 paramagnetic impurities.

The results of these measurements[12] appear in Table I. In order to compare these values, the molar susceptibility is given counting two atoms as one "molecule" for the elemental semiconductors. With use of these data, calculated values for χ_c, and literature values for E_g, α, and $d\epsilon(0)/dT$, the quantities χ_v and χ_p could be determined separately as shown in Table II. It is interesting to note that χ_v and χ_p are large compared with χ_c and that these terms nearly cancel one another in the case of Group-IV semiconductors. We come back to this point later when we discuss results on amorphous Ge.

From χ_v one obtains an average diamagnetic valence radius

$$r_L = \Big(\sum_{\text{valence}} \langle r^2\rangle\Big)^{1/2}$$

which is compared with the interatomic separation d in Table III. The ratio is the same within experimental error for all materials measured. This justifies our assumption of using α for the temperature coefficient of r_L. Calculations[6] of χ_v from electron density distributions for the case of GaAs agree well with our measurements. This indicates that the values of Table III are reasonable.

It seems significant that this simple model can

TABLE III. Interatomic distance d and average diamagnetic valence radius r_L.

	d (Å)	r_L (Å)	$2r_L/d$
C	1.548	1.04 ± 0.15	1.34 ± 0.19
Si	2.346	1.32 ± 0.10	1.13 ± 0.09
Ge	2.450	1.48 ± 0.06	1.21 ± 0.05
GaAs	2.441	1.46 ± 0.04	1.20 ± 0.03
GaP	2.360	1.43 ± 0.04	1.21 ± 0.03

TABLE IV. Average magnetic matrix element.

	B (10^{-4} eV cm^3/mole)
C	1.8 ± 0.6
Si	1.8 ± 0.3
Ge	2.2 ± 0.2
GaAs	1.6 ± 0.1
GaP	1.6 ± 0.1

explain the small negative $d\chi_L/dT$ of diamond. It is due to the first term in Eq. (5). The second term is positive because $d \ln E_g/dT < 0$.

The average magnetic matrix element B is nearly the same for the materials studied as shown in Table IV. Here we set $\beta = 1$. This agrees with our argument which led to Eq. (4), and which concluded that B depends more on the charge density symmetry than on the bond strength. The fact that diamond fits into this scheme is remarkable because its gap E_g is significantly different from those of the other materials.

The diamagnetic susceptibility of Ge depends very much on whether the material is amorphous or crystalline. Amorphous Ge is 2.7 times more diamagnetic than crystalline Ge.[13] This is a unique occurrence. For a large number of semiconductors studied, for example Se, S, As_2S_3, and As_2Se_3, the values of χ are the same in the amorphous and crystalline state to within experimental error (a few percent). We believe that disorder-induced changes in bond angles and lengths which affect the values of χ_v and χ_p will produce a large relative change of χ_L particularly in Ge where large values of χ_v and χ_p very nearly cancel. We are presently studying χ and $d\chi/dT$ of the other tetrahedral semiconductors in the amorphous state. Preliminary results show that also amorphous Si is appreciably more diamagnetic than crystalline Si.

It appears that the magnetic susceptibility is, like the electric susceptibility, a valuable tool for studying chemical bonding in semiconductors.

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