cedure leaves unfilled closely spaced states near the top of the valence band which reflect the elastic artifacts of the surfaces. The energy difference they quote (3.3 eV) between the total energy with the vacancy in the 000 and in the $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ positions in silicon would probably be substantially less if they followed our procedure. (In the case of the vacancy in diamond, we find our procedure reduces the difference by a factor of 2.)

Our procedure gives a net charge of $-36e$ to a 35-carbon-atom cluster. However, this has no effect at all on the energy levels because the EHT treatment is not a self-consistent one. The molecular-orbital wave functions and energies are independent of the way in which we populate them after the calculation. Actually, however, a Mulliken population analysis does reveal some physical significance to our procedure. One finds that the charge is closely neutral for the central atom and its nearest neighbors. The charge of the atoms in the next two shells (which have one neighbor missing) is $\sim - e$, and in the outer shell

(with two missing neighbors) is $\sim - 2e$. In effect, we have put an additional electron in each "dangling bond" to saturate it and to simulate the electron contributed by the missing neighbor in the large bulk crystal. If these neighbor atoms were present the extra charges would be on them, and in this sense the charge density is indeed "uniform" on our cluster.

In conclusion, we agree that the EHT method is one that can and should be improved. The surfaces undoubtedly provide complications and it would be desirable to move them farther out by using a larger cluster, or get rid of them entirely by appropriate boundary conditions. However, we believe that the basic EHT approach and the finite cluster, when handled as clarified above, may represent a considerably better approximation to the deep-level problem that is indicated in points (iii) and (iv) of Moore and Carlson. This confusion is no doubt due to the rather terse description of our procedures necessitated by the form of our preliminary communications.[2-4]

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Paramagnetostriction of Transition Metals

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Some recent measurements of paramagnetostriction of transition metals are analyzed taking in account the over-all symmetry of the effect, and the possibility of shape paramagnetostriction. It is suggested that the anisotropic effect can explain the rather large experimental values obtained, and that either orbital paramagnetism, or spin-orbit coupling, must be responsible for shape effects.

Some recent measurements of paramagnetostriction of transition metals by Fawcett[1,2] have resulted in surprisingly high values for some metals. For example, the reported values of $\partial \ln\chi/\partial \ln V$ are 14 for Mo, 6.5 for W, 9.6 for Rh, and 22 for Ir. The purpose of this note is to suggest that the interpretation of the measured values in terms of volume dependence of susceptibility is too restrictive, and that one must take in account the tensor character of the phenomenon.

Let us write the free energy of an "initial" volume unit of a metal, assuming cubic symmetry,

$$U = U_0 + \tfrac{1}{2}C_{11}(e_{xx}^2 + e_{yy}^2 + e_{zz}^2) + C_{12}(e_{yy}e_{zz} + e_{zz}e_{xx} + e_{xx}e_{yy}) + \tfrac{1}{2}C_{44}(e_{yz}^2 + e_{zx}^2 + e_{xy}^2)$$

$$-d_{11}(e_{xx}H_x^2+e_{yy}H_y^2+e_{zz}H_z^2)-d_{12}[(e_{yy}H_z^2+e_{zz}H_y^2)+(e_{zz}H_x^2+e_{xx}H_z^2)+(e_{xx}H_y^2+e_{yy}H_x^2)]$$

$$-d_{44}(e_{yz}H_yH_z+e_{zx}H_zH_x+e_{xy}H_xH_y)-\tfrac{1}{2}\chi_0(H_x^2+H_y^2+H_z^2) . \tag{1}$$

The e_{ij} are the Voigt components of the strain tensor, C_{11}, C_{12}, and C_{44} are the elastic moduli, and χ_0 is the magnetic susceptibility of an undeformed crystal, which, in a cubic system, must be a scalar. The coupling between magnetic and elastic effects, which is taken linear in e_{ij}, is described by a term which must be quadratic in H, even in a noncentrosymmetric system, in order to preserve the time-reversal invariance. The coefficients of this coupling term are the components of a fourth-order tensor, which for cubic symmetry reduces to three independent ones, described in a quasi-Voigt notation by d_{11}, d_{12}, and d_{44}.

From (1), one gets the components of the susceptibility tensor for a strained crystal:

$$\chi_{11}=\chi_0+2(d_{11}-d_{12})e_{11}+2d_{12}\Delta V/V, \tag{2}$$

$$\chi_{23}=d_{44}e_{23} .$$

The strain tensor, in the presence of magnetic field, becomes

$$e_{11}=\alpha_3 H_1^2+\tfrac{1}{3}(\alpha_1-\alpha_3)\vec{H}^2 , \tag{3}$$

$$e_{23}=\alpha_5 H_2 H_3 ,$$

where

$$\alpha_1=(d_{11}+2d_{12})/(C_{11}+2C_{12}) ,$$

$$\alpha_3=(d_{11}-d_{12})/(C_{11}-C_{12}) , \tag{4}$$

$$\alpha_5=d_{44}/C_{44} .$$

The α_i coefficients are associated with the Γ_i representations of the cubic group in Bethe notation. The analysis of Fawcett assumes $\alpha_3=\alpha_5=0$, which automatically neglects parts of the effect due to the coefficients belonging to tetrahedral (Γ_3) or trigonal (Γ_5) representations.

If a magnetostriction experiment is made on a single crystal, taking as coordinate axes the axes of the crystal in the absence of magnetic field, and taking $\vec{\eta}$ as the unit vector along the magnetic field, $\vec{\lambda}$ as unit vector in the direction of observation, and γ as the angle $(\vec{\eta}, \vec{\lambda})$, one obtains

$$\frac{1}{H^2}\left(\frac{\Delta l}{l}\right)_{\vec{\lambda}}=\tfrac{1}{3}(\alpha_1-\alpha_3)$$

$$+(\alpha_3-\tfrac{1}{2}\alpha_5)\sum_{i=1}^{3}\lambda_i^2\eta_i^2+\tfrac{1}{2}\alpha_5\cos^2\gamma . \tag{5}$$

Fawcett has worked on samples of cylindrical shape, with $\vec{H}$ parallel with the sample axis. He measured the elongation $\Delta l/l$. In another experi-

ment on palladium alloys, Keller et al.[3] measured in addition to the above change of radius $\Delta r/r$. In a polycrystalline sample one may assume the interaction between crystallites to be only slightly disturbed by the magnetoelastic forces, and assuming a spherical distribution of crystallites, one gets from (5)

$$(1/H^2)(\Delta l/l)=\tfrac{1}{3}\alpha_1+\tfrac{4}{15}\alpha_3+\tfrac{1}{5}\alpha_5 ,$$

$$(1/H^2)(\Delta r/r)=\tfrac{1}{3}\alpha_1-\tfrac{2}{15}\alpha_3-\tfrac{1}{10}\alpha_5 ,$$

or, in Keller's notation,

$$S_v=\frac{1}{H^2}\frac{\Delta V}{V}=\alpha_1 ,$$

$$S_f=\frac{1}{H^2}\left(\frac{\Delta l}{l}-\frac{\Delta r}{r}\right)=\tfrac{2}{5}\alpha_3+\tfrac{3}{10}\alpha_5 .$$

Similarly for a polycrystalline sample, one gets a scalar susceptibility

$$\chi=\chi_0+2\kappa\alpha_1\Delta V/V ,$$

where κ is the compressibility modulus. Using Keller's data for palladium $S_v=95\times10^{-18}$ Oe^{-2} and $S_f=-83\times10^{-18}$ Oe^{-2} one gets $\partial \ln\chi/\partial \ln V=4.4$, instead of Fawcett's value of -3.4. The absolute change is important and may explain surprisingly high values for other metals.

The explanation of the shape effect, using the standard model of a transition metal, where susceptibilities—and Knight shifts[4]—add without interaction, is to be looked for in the orbital susceptibility or in the spin-orbit coupling. Indeed, in (2), without spin-orbit forces, the spin susceptibility is due to a repopulation of levels, the axis of quantization of a spin is arbitrary, and so χ must be a scalar. Consequently (3) implies that $\alpha_3=\alpha_5=0$ and thus $d_{11}-d_{12}=0$ and $d_{44}=0$.

The same kind of symmetry may be used to understand the effect of strain on the Knight shift, which is a second-order tensor, like susceptibility. From our measurements on cold-worked Rh powders,[5,6] one could have deduced, neglecting the Γ_3 and Γ_5 contributions, that $\partial \ln K/\partial \ln V \sim 40$, taking as reference organic complexes as suggested by Brown and Green.[7] Since this is much too large, one must take into account the anisotropic effects.

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Thickness Dependence of the Ground-State Exciton Energy in WSe₂ [†]

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A theory developed for a thin anisotropic semiconductor, where the exciton is treated in the effective-mass approximation and where the effect of crystal surfaces is included by means of image-charge potentials, is applied to crystals of thickness less than 500 Å. The theory leads to an exciton ground-state energy which closely approaches an inverse-square-law dependence on thickness. By the use of estimates of the dielectric and reduced-exciton-mass components quantitative agreement with data on WSe₂ is obtained.

Recent developments in the theory of the effect of finite crystal size on the exciton-energy spectra have been made by Jones and Brebner[1] (hereafter called I) and Bendow.[2] Both these papers use image potentials to account for the effect of the surfaces on the exciton- and impurity-electron systems, respectively. In the present paper we utilize the theory of I in making a comparison with the recent experimental data of Consadori and Frindt[3] on the exciton-absorption spectrum in very thin crystals of WSe₂.

The Schrödinger equation for an exciton in a uniaxial crystal with the z direction along the c axis and normal to the plane-parallel interfaces a distance $2L$ apart is, in transformed coordinates,[4]

$$\frac{-\hbar^2}{2\mu_\perp}\nabla_{r'}^2\Psi - \frac{\hbar^2}{2M_\perp}\left(\frac{\partial^2}{\partial X'^2}+\frac{\partial^2}{\partial Y'^2}\right)\Psi - \frac{\hbar^2\beta^2}{2M_\parallel}\frac{\partial^2}{\partial Z'^2}\Psi - \left[\frac{e^2}{4\pi\epsilon_0[\epsilon_\perp\epsilon_\parallel(x'^2+y'^2+\gamma'^2z'^2)]^{1/2}} - U_L' - U_R'\right]\Psi = E\Psi ,$$

$$(1)$$

where

$$\gamma=\left(\frac{\epsilon_\perp\mu_\perp}{\epsilon_\parallel\mu_\parallel}\right)^{1/2} , \quad \beta=\left(\frac{\mu_\parallel}{\mu_\perp}\right)^{1/2} .$$

$\vec{r}'(x', y', z')$ and $\vec{R}'(X', Y', Z')$ are the relative and center-of-mass coordinates, respectively, of the exciton. U_L' and U_R' are the image-charge potentials; these and other quantities are defined in I.

We neglect the contribution from the center of mass in the X' and Y' directions and write

$$\Psi=\phi_n(x', y', z', Z')F(Z') . \qquad (2)$$

On separation under the adiabatic approximation we obtain for the case $\gamma=1$

$$-\nabla_t^2\phi_n - (2/t - U_L'' - U_R'')\phi_n = \xi_n(D')\phi_n , \qquad (3)$$

$$-\frac{d^2F}{dD'^2}+\left(\frac{M_\parallel}{\mu_\parallel}\right)[\xi_n(D') - G]F = 0 , \qquad (4)$$

where

$$t=r'/a_0 , \quad D'=Z'/a_0 , \quad a_0=4\pi\hbar^2\epsilon_0(\epsilon_\perp\epsilon_\parallel)^{1/2}/\mu_\perp e^2$$

is the effective exciton Bohr radius. The quantities denoting energy in Eqs. (3) and (4) are now expressed in exciton-rydberg units, having been multiplied by T where

$$T = 8\pi\epsilon_0(\epsilon_\perp\epsilon_\parallel)^{1/2}a_0/e^2 \qquad (5)$$

and, in particular,

$$U_i'' = U_i'T \quad (i=L, R) .$$

Since we are interested here in the ground-state exciton, we need only consider the case $n=1$ and employ the trial wave function (see I)