Magnetic susceptibility of metallic transition-metal dichalcogenides

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A tight-binding model has been used to estimate the anisotropy of the magnetic susceptibility of the metallic transition-metal dichalcogenides. The calculated anisotropies obtained are in qualitative agreement with experiment and can be interpreted in terms of the electronic structure of these compounds. It is expected that these results will make possible a more detailed interpretation of the changes in magnetic susceptibility which occur in these compounds upon transforming to a charge-density-wave state.

Periodic solids which undergo transitions to states characterized by a periodicity incommensurate with that of the underlying lattice have received considerable attention in recent years.[1] One frequently studied class of systems is the metallic transition-metal dichalcogenides, most of which transform to charge-density-wave (CDW) states at sufficiently low temperature.[2] In part because of the complicated electronic structure of these layered compounds, a quantitative microscopic understanding of the normal-state conditions which control the occurrence of the transition, and of the changes in electronic structure which accompany the transition when it occurs, is still not available. One experimentally accessible quantity which depends sensitively on the electronic structure in the vicinity of the Fermi energy[3] is the magnetic susceptibility χ of the metal. For metals with a high Fermi-level density of states $D(\epsilon_F)$, χ is dominated by the paramagnetic Pauli component χ_P; in the absence of exchange enhancement and spin-orbit coupling, $\chi_P(T)$ is isotropic and proportional to the average density of states within $\sim k_B T$ of the Fermi level. As a result, measurement of $\chi(T)$ would seem to probe the electronic structure in the region of interest and offer the possibility of discriminating between different models of the CDW state in a given material. However, as first pointed out by Benchimal et al.,[4] χ is very anisotropic in some transition-metal dichalcogenides. This fact confuses considerably the interpretation of χ data and its comparison with other data.[4-6] In this article, we report on an attempt to eliminate this confusion by using a tight-binding model to describe the essential features of the electronic structure and to give the first theoretical estimates of the anisotropy of χ_P in both the $1T$ and $2H$ polytypes of these metallic layered compounds.

The transition-metal dichalcogenide (MX_2) compounds are composed of weakly interacting sand-wiches with each sandwich consisting of a hexagonally packed layer of M atoms between hexagonally packed layers of X atoms. The electronic structure, at a first approximation, consists of metallic d bands lying between metal-chalcogen s-p bonding and antibonding bands. If M is a Group-VB transition metal, the s-p bonding bands are full and the Fermi level lies in the M d bands. For our purposes, we can therefore ignore the s-p bands and adopt a model Hamiltonian of the form

$$H = H_{TB} + H_{SO} ,\qquad (1)$$

where H_{TB} is a tight-binding parametrization of the M d bands and H_{SO} is the spin-orbit interacton. This model is in the same spirit as that adopted by Friedel et al.[7] and has recently been used by Rahman et al.[8] as the basis of a calculation of the g tensor in palladium. For H_{TB} we use the Slater-Koster linear-combination-of-atomic-orbitals (LCAO) fits obtained by Mattheis[9] in fitting his augmented plane-wave (APW) band structure. The spin-orbit coupling parameter, λ, necessary to specify H_{SO}, can be estimated by comparison with atomic and pure-metal values (see below).

In considering the magnetic susceptibility of this model system, we follow the development of Misra and Kleinman.[10] These authors have shown that the magnetic susceptibility of a system of Bloch electrons can be regarded as the sum of two terms, one coming from changes in single-particle energies quadratic in the magnetic field and the other coming from the splitting of the Kramers degeneracy of the Bloch states near the Fermi level, which is linear in the magnetic field. It is this latter contribution which is the natural generalization to the spin-orbit coupling case of the Pauli susceptibility. For a field applied in

the α direction, it may be written as

$$\chi_P^g = -\frac{\mu_B^2}{2} \sum_{n,\vec{k}} (g_{n,\vec{k}}^\alpha)^2 f'(E_{n,\vec{k}}) \quad , \tag{2}$$

where $E_{n,\vec{k}}$ is the Bloch eigenvalue in the absence of the field

$$(g_{n,\vec{k}}^\alpha)^2 = 4(|\langle n,\vec{k},+|\mu_\alpha|n,\vec{k},+\rangle|^2$$

$$+ |\langle n,\vec{k},+|\mu_\alpha|n,\vec{k},-\rangle|^2) \quad ; \tag{3}$$

$|n,\vec{k},\lambda\rangle$ $(\lambda = \pm)$ is one of the Kramers degenerate states with wave-vector label $\vec{k}$ and band label n and μ_α is the periodic part of the magnetic moment operator.[10,11] In order to evaluate Eq. (3), we require the matrix elements of μ_α between our basis states which are products of tight-binding orbital functions and the eigenstates of σ_Z. In this tight-binding limit, we have[12]

$$\langle i,\vec{k},\sigma|\mu_\alpha|i',\vec{k},\sigma'\rangle = \langle i|L_\alpha|i'\rangle \delta_{\sigma,\sigma'} + \delta_{i,i'}\langle\sigma|\sigma_\alpha|\sigma'\rangle \quad , \tag{4}$$

where $\langle i|L_\alpha|i'\rangle$ is the readily calculated matrix ele-

ment of the appropriate orbital angular momentum operator between the angular parts of the tight-binding basis functions and $\langle\sigma|\sigma_\alpha|\sigma'\rangle$ is a Pauli spin matrix element.

In evaluating Eq. (2), we have taken advantage of the nearly two-dimensional nature of the electronic structure by using a two-dimensional analog of the tetrahedron method[13] combined with Gaussian quadrature in the z direction to perform the integrals over the hexagonal Brillouin zones of the $1T$ and $2H$ structures.[14] The eigenvalues and eigenvectors of H were obtained by using standard matrix techniques to diagonalize the Hamiltonian matrix in the tight-binding representation. Equation (3) was then evaluated at each $\vec{k}$ point in our Brillouin zone grid by using Eq. (4) and the expansion coefficients of the eigenfunctions. The results obtained for $\chi_P(T=0)$ for some $1T$ and $2H$ polytypes of the MX_2 compounds are listed in Table I,[15-17] for fields applied both parallel ($\chi_P^\parallel$) and perpendicular ($\chi_P^\perp$) to the planes of the X-M-X sandwiches. In discussing the comparison of these results with the experimental susceptibilities listed in Table I we consider the $2H$ polytypes first. For this structure χ_P, is clearly strongly exchange-enhanced as we would expect on the basis of the $D(\epsilon_F)$ calculated here and metallic values for the density-functional Stoner parameter.[14,18,19] Since this exchange enhancement is nearly

TABLE I. Results for χ_P. $D(\epsilon_F)$ is in units of electron states per M atom per Ry. All susceptibilities are in units of $(10^3 \text{ kg})^{-1}$. For the $2H$ polytypes the experimental χ is dominated by χ_P which is strongly exchange enhanced. We therefore compare $\chi_P^\perp/\chi_P^\parallel$ to the experimental $\chi^\perp/\chi^\parallel$. For the $1T$ polytypes χ has a dominant diamagnetic component and we compare $\chi_P^\parallel - \chi_P^\perp$ to the experimental $\chi^\perp - \chi^\parallel$. The experimental results are for Se chacogen atoms but this is of no importance at the present level of description. The λ value chosen were 20 mRy for Ta, 10 mRy for Nb, and 4 mRy for V. In modeling $1T$-VSe$_2$ we used the same H_{TB} as in $1T$-TSe$_2$.

Metal	$2H$-TaSe$_2$	$2H$-NbSe$_2$	$1T$-TaSe$_2$	$1T$-VSe$_2$
$D(\epsilon_F)$	39	57	18	17
$\langle(g^\perp)^2(\epsilon_F)\rangle/4$	0.92	1.06	0.39	0.86
$\langle(g^\parallel)^2(\epsilon_F)\rangle/4$	0.23	0.41	0.71	0.95
$\chi_P^\perp$	0.25	0.57	0.05	0.11
$\chi_P^\parallel$	0.06	0.22	0.09	0.12
$\chi^\perp$(expt)	1.0[a]	1.3[b]	-0.14[c]	0.78[d]
$\chi^\parallel$(expt)	0.4[a]	0.7[b]	-0.10[c]	0.78[d]
$\chi_P^\perp/\chi_P^\parallel$	4.0	2.6		
$\chi^\perp/\chi^\parallel$(expt)	2.5	1.8		
$\chi_P^\parallel - \chi_P^\perp$			0.04	0.01
$\chi^\perp - \chi^\parallel$(expt)			0.04	0.00

[a] Reference 4. [b] Reference 15. [c] Reference 16. [d] Reference 17.

isotropic,[14] we can compare experimental and theoretical values of $\chi_P^\perp/\chi_P^\parallel$. The agreement is seen to be quite acceptable considering the approximate nature of this model. For the $1T$ structure, $D(\epsilon_F)$ is much lower and χ_P is not strongly exchange enhanced. As a result χ_P does not dominate χ in these compounds and they are, for the most part, diamagnetic. Since the diamagnetic contribution to χ comes from both core and valence electrons, it is not likely to be very anisotropic and we can compare the theoretical values of $\chi_P^\perp - \chi_P^\parallel$ with experimental values of $\chi^\perp - \chi^\parallel$; again the agreement is acceptable.

It is possible to give a simple physical interpretation of the results we have obtained. We first consider the ligand-field model obtained by setting the intra-atomic terms in H_{TB} to zero.[20] In both polytypes, the three lowest d states may be regarded as a t_{2g} level with a small splitting between the $|l,m\rangle = |2,0\rangle$ state and the doubly degenerate $|2,\pm2\rangle$ manifold. Because the coordination of the M atoms by the X atoms is nearly octahedral, the energy splitting is much smaller in the $1T$ structure. (In Mattheiss fit, the splitting is 11 mRy in $1T\text{-TaS}_2$ and 41 mRy in $2H\text{-TaS}_2$.) When the spin-orbit interaction is applied, the $|2,\pm2\rangle$ mainifold is split by $\sim2\lambda$ with $g^\parallel$ being zero for both levels; $g^\perp \sim 2-4 = -2$ and $2+4=6$ for lower and upper levels, respectively, with the second term coming from the orbital contribution to the magnetic moment in each case. For the $|2,0\rangle$ level, $g^\perp = 2$ and $g^\parallel \sim 2 - 12\lambda/\Delta\epsilon$ where $\Delta\epsilon$ is the energy
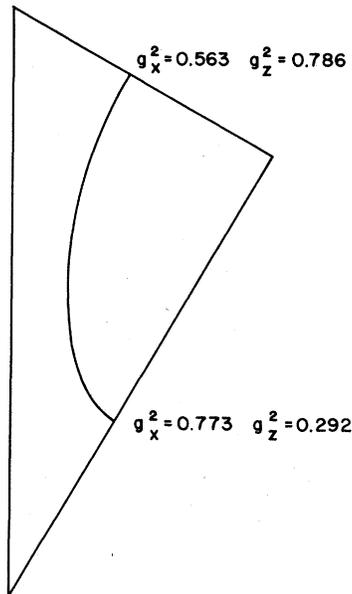
gap between the $|2,0\rangle$ level and the $|2,\pm1\rangle$ manifold. ($\Delta\epsilon = 198$ mRy for $1T\text{-TaS}_2$ and 133 mRy for $2H\text{-TaS}_2$.) When the interatomic terms in H_{TB} are included, the energy levels broaden into bands with strong hybridization of $|2,0\rangle$ and $|2,\pm2\rangle$ levels and, in the absence of spin-orbit interactions, the orbital contribution to the g factors is quenched. The Fermi level lies at the point where 0.5 electron states per spin per M atom are occupied. In the $2H$-structure at the Fermi energy, the $|2,0\rangle$ levels are hybridized nearly equally with the upper and lower states of the spin-orbit split $|2,\pm2\rangle$ manifold in such a way that $\langle(g^\perp)^2(\epsilon_F)\rangle$ is ~2 while $\langle(g^\parallel)^2(\epsilon_F)\rangle$ is reduced in accordance with its low value in all three states. In the $1T$ structure the reduction of $\langle(g^\parallel)^2(\epsilon_F)\rangle$ is smaller because of the higher value of $\Delta\epsilon$. Furthermore, since the lower of the spin-orbit-split $|2,\pm2\rangle$ states is nearly degenerate with the $|2,0\rangle$ state, it has a much higher weight at the Fermi level than the upper $|2,\pm2\rangle$ state. It is the partial quenching of the orbital contribution to $g^\perp$ for this state (see above) that leads to the low value of $\langle(g^\perp)^2(\epsilon_F)\rangle$ for the $1T$ structure. While some features of the above argument are necessarily qualitative, it is consistent with the partial densities of states we have calculated[14] and we believe that is an accurate description of the physics behind the results for the χ_P anisotropy which we have obtained in this model.

In summary, this tight-binding model calculation appears to capture all the qualitative features of the χ anisotropy in the metallic MX_2 compounds, namely: (i) The anisotropy is more pronounced in compounds with high-Z M atoms; (ii) the susceptibility is more paramagnetic for fields applied perpendicular to the
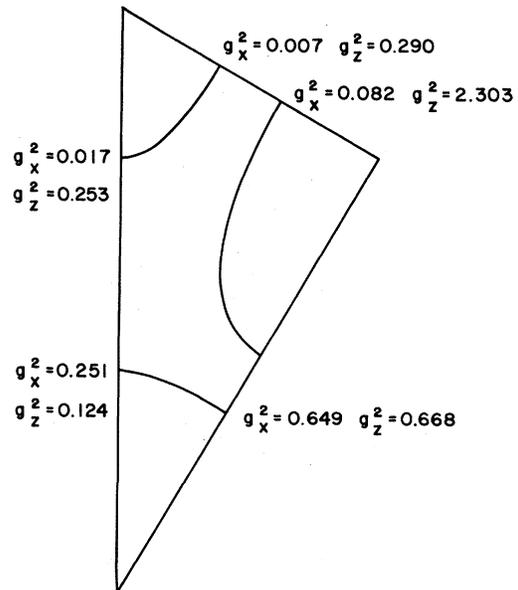

FIG. 1. Fermi-surface intersection with a plane parallel to the layers for $1T\text{-TaSe}_2$. The variation of the g factor over the surface is indicated for two directions of applied field; one parallel to the layers $(g_x{}^2)$ and one perpendicular to the layers $(g_z{}^2)$. Only one "irreducible" region of the hexagonal Brillouin zone is illustrated.

FIG. 2. As in Fig. 1 but for $2H\text{-TaSe}_2$.

layers in the $2H$ polytypes; and (iii) the susceptibility is more paramagnetic for fields applied parallel to the layers in the $1T$ polytypes. Confidence in the model could be further enhanced by test of more detailed predictions of the model, such as the variation of the g factors over the Fermi surfaces in $1T$ and $2H$ polytypes shown in Figs. 1 and 2.

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