

ARTICLES

Band structure and transport properties of CrO₂

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The local-spin-density approximation is used to calculate the energy bands of both the ferromagnetic and paramagnetic phases of metallic CrO₂. The Fermi level lies in a peak in the paramagnetic density of states, and the ferromagnetic phase is more stable. As predicted by Schwarz, the Fermi level lies in an insulating gap in the minority-spin bands between oxygen *p* and chromium *d* states (“half-metallic” behavior). The resulting magnetic moment is $2\mu_B$ per Cr atom, in agreement with experiment. The A_{1g} Raman frequency is predicted to be 587 cm^{-1} . Drude plasma frequencies are of order 2 eV, as seen experimentally by Chase. The measured resistivity is used to find the electron mean free path ℓ , which is only a few angstroms at 600 K, but, nevertheless, resistivity continues to rise as temperature increases. This puts CrO₂ into the category of “bad metals” in common with the high- T_c superconductors, the high- T metallic phase of VO₂, and the ferromagnet SrRuO₃. In common with both SrRuO₃ and Sr₂RuO₄, the measured specific-heat parameter γ is higher than band theory predicts by a renormalization factor close to 4.

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I. INTRODUCTION

The physical properties of rutile-structure oxides are diverse, including insulators (TiO₂), antiferromagnets (MnO₂), good metals (RuO₂), and metal-insulator systems (VO₂). Metallic CrO₂, with a Curie temperature $T_{\text{Curie}} \approx 390\text{ K}$, is the only ferromagnet in this class. Schwarz¹ used local-spin-density-approximation (LSDA) band theory to predict that the spin moment would be the full $2\mu_B$ required by Hund’s rules for the Cr⁴⁺ ($3d^2$) ion. The Fermi level lies in a partly filled (metallic) band for the majority (up-spin) electrons, but for minority (down) spins lies in a semiconducting gap which separates the filled oxygen *p* levels from the chromium *d* levels. The situation where one spin species is metallic and the other semiconducting has been named “half-metallic” by de Groot *et al.*² Brändle *et al.*³ found good agreement between theory and experiment for the diagonal parts of the optical conductivity tensor. The off-diagonal magnetoconductivity properties were recently calculated by Uspenskii, Kulatov, and Halilov,⁴ who obtained reasonable agreement with experiment. Evidence of close to 100% spin polarization was seen in both spin-polarized photoemission⁵ and vacuum tunneling.⁶ However, this polarization was observed not at the Fermi energy, but 2 eV below, a discrepancy which has not yet been resolved.

Besides the paper by Schwarz,¹ LSDA band-structure calculations have been reported by several other groups.⁷⁻⁹ The band structure of Ref. 8 is in good agreement with that of

Schwarz; however, Refs. 7 and 9 give somewhat different results. Reference 7 finds a gap between oxygen *p* and chromium *d* states for *both* spin species, whereas Schwarz only finds a gap for minority spins. In Ref. 9 the computed spin moment is $1.772\mu_B$, which is inconsistent with the half-metallic picture. We perform further investigations of this material within the LSDA using a plane-wave pseudopotential (PWPP) method, and obtain majority- and minority-spin bands that agree well with the all-electron calculations of Schwarz and Ref. 8, rather than those of Refs. 7 and 9. Our calculations predict the frequency of the $Q=0$ Raman-active optic mode of A_{1g} symmetry, and provide an analysis of transport measurements using band-theoretical parameters. This work is one of the first illustrations of the ability of a plane-wave pseudopotential technique to do a high-precision LSDA calculation, and the first, to our knowledge, for a ferromagnetic compound.

II. COMPUTATIONAL METHOD

The electronic ground state for CrO₂ is computed using the local-spin-density approximation¹⁰ of density-functional theory.¹¹ The form chosen for the exchange-correlation energy and potential is that of Ceperley and Alder.¹² We use the frozen-core approximation, in which the core electrons are fixed in their free-atom configuration, and only the valence electrons are allowed to respond to the chemical environment of the solid. Interactions between the valence elec-

trons and ion cores are described by efficient,¹³ norm-conserving pseudopotentials.¹⁴ The s , p , and d pseudopotential cutoff radii are 1.10, 1.00, and 1.50 bohr, respectively, for chromium, and 1.25, 1.25, and 1.25 bohr, respectively, for oxygen. Single-particle wave functions are expanded in a plane-wave basis set¹⁵ which is well converged for CrO_2 at a cutoff energy of 81 Ry. The use of pseudopotentials and plane waves to study nonmagnetic materials within local-density-functional theory has been extremely successful for a wide range of systems,¹⁶ including transition-metal oxides.¹⁷ Application of this method to magnetic systems, however, is less well established. One of the goals of this study is to demonstrate its validity in the realm of magnetic compounds.

A worry with using the PWPP method for magnetic materials is that, because spin splitting of the exchange-correlation potential is driven largely by the tightly bound d electrons, spin-polarizing effects would be prominent in the core region, where the pseudo wave-functions differ significantly from the all-electron wave functions. However, Sasaki, Rappe, and Louie recently demonstrated¹⁸ that this is not, in fact, a problem. While the pseudopotential approach does cause the $3d$ wave function to shift in the core region relative to the all-electron case, it also produces a similar shift in the spin splitting of the exchange-correlation potential. Thus the total energy, which involves integration of the density against the potential, is largely unaffected. Sasaki, Rappe, and Louie,¹⁸ as well as Cho and Kang,¹⁹ have also shown that it is important to employ the partial-core correction scheme of Louie, Froyen, and Cohen²⁰ in order to reduce core-valence overlap errors introduced by nonlinearity of the exchange-correlation potential. Spin-polarized calculations using this method have been performed for iron¹⁸ and nickel,^{18,19} and the agreement with all-electron LSDA calculations for structural, electronic, and magnetic properties is outstanding.

To our knowledge, the present study of CrO_2 is the first LSDA investigation of a ferromagnetic compound using the PWPP method. Results for the magnetic and electronic structure obtained here are in excellent agreement with previous all-electron LSDA band-structure calculations of this system,^{1,8} which nicely illustrates the effectiveness and precision of this method.

The rutile structure (see Fig. 1) has a simple tetragonal Bravais lattice with two formula units per unit cell. It consists of chromium atoms octahedrally coordinated by oxygen atoms, with the oxygen octahedra arranged in “ribbons” running parallel to the tetragonal c axis. Adjacent octahedra on the same ribbon share a common edge, whereas octahedra on adjacent ribbons share a common corner and are situated relative to each other according to a fourfold screw axis with nonprimitive translation equal to half the c axis. Figure 1 highlights the planar CrO_4 units which form the ribbons. We refer to the ribbon oxygens as “equatorial,” and the other two oxygens of the CrO_6 octahedra as “apical.” The octahedra are orthorhombically distorted away from the ideal geometry, with the apical oxygen atoms slightly more distant from the central chromium atom than the equatorial oxygen atoms. Chromium atoms are located at the positions $[0,0,0]$ and $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ in lattice coordinates, and the four oxygen atoms are located at $[u, u, 0]$, $[1-u, 1-u, 0]$, $[\frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2}]$, and

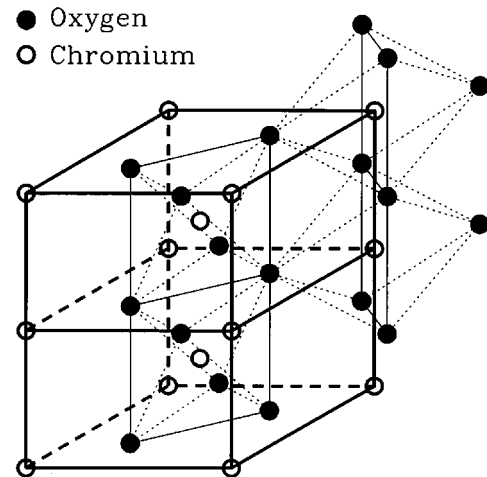


FIG. 1. Illustration of the rutile structure. Heavy solid and dashed lines demarcate unit cells of the crystal. Thin lines emphasize the oxygen octahedra surrounding each chromium atom, with solid lines highlighting the equatorial planes and dotted lines linking them to the apical oxygen atoms.

$[\frac{1}{2}-u, \frac{1}{2}+u, \frac{1}{2}]$, where u is a dimensionless internal coordinate less than unity. The measured values of the structural parameters a , c , and u are 4.419 Å, 2.912 Å, and 0.303, respectively.²¹ In the present study, we have fixed the axes at their experimental lengths, and optimized the internal coordinate, u . Its computed value is 0.3043, in excellent agreement with experiment.

The irreducible wedge of the tetragonal Brillouin zone has been sampled at nine k points for the purposes of computing the self-consistent electron density. A high degree of convergence for this level of sampling has been confirmed by redoing the calculation for a given structure using 24 k points. The two calculations agree to within 0.5 mRy per CrO_2 formula unit. It may seem surprising that so few k points are needed to achieve convergence, since LSDA calculations for Fe and Ni require many more (40–60 k points).¹⁸ The main reason for the good k -point convergence for CrO_2 is the insulating nature of the minority bands. It is well known that insulating bands stabilize the charge density at a low number of k points. It helps that the rutile unit cell, containing six atoms in a fairly open structure, is considerably larger than the monatomic unit cells of close-packed metals. Thus a similar density of k points could be obtained with a smaller total number of k points. The electronic density of states, magnetic moment, Fermi energy, Fermi surface area, and transport coefficients are determined using the linear tetrahedron method²² on band energies computed at 50 irreducible k points.

III. ELECTRONIC STRUCTURE

Figure 2 shows the computed electronic density of states (DOS) of ferromagnetic CrO_2 for majority spins (positive axis) and minority spins (negative axis). These results agree well with earlier DOS calculations for this material.^{1,8} Integrating the total DOS up to the total number of valence electrons determines the Fermi level, which is then used as the zero of energy. The Fermi level intersects the majority-spin

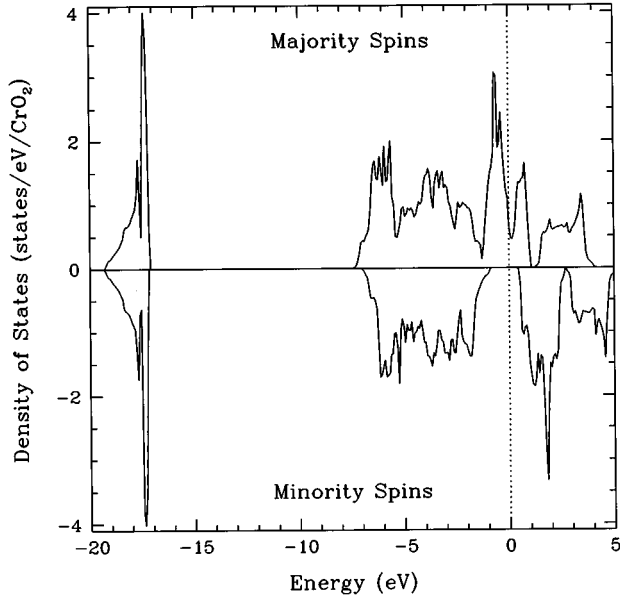


FIG. 2. Densities of states for majority and minority spins in ferromagnetic CrO₂. Majority (minority) states are plotted along the positive (negative) ordinate. The dotted line denotes the Fermi energy.

bands near a local minimum in the DOS, and lies in a band gap of the minority-spin DOS. Thus CrO₂ is half-metallic within LSDA, as was first demonstrated by Schwarz.¹ This property leads to an integral magnetic moment, which is found to be $2\mu_B/\text{CrO}_2$, the value predicted by Hund's rules for the spin moment of the Cr⁴⁺ ion. This agrees with the measured saturation moment per formula unit for CrO₂ of $2.0\mu_B$,^{23,24} which is nearly all attributable to spins; Uspenskii, Kulatov, and Halilov⁴ calculated an orbital contribution of a few percent. The density of majority states at the Fermi level is 0.69 states/eV/CrO₂.

Contour plots for the spin density [$s(\vec{r}) = n_{\uparrow}(\vec{r}) - n_{\downarrow}(\vec{r})$] are shown in Fig. 3 for two cross sections of the crystal. Figure 3(a) contains the (1 $\bar{1}$ 0) plane formed by the equatorial oxygen atoms and the chromium atom. Figure 3(b) shows a perpendicular plane containing two apical and two equatorial oxygen atoms. Both panels have the same contour-level spacing. These figures reveal that the spin density is highly localized around the chromium atom, and that it stems almost exclusively from the chromium 3d states. Figure 3(a) shows that the spin density has the ‘‘cloverleaf’’ shape of a d_{xy} function, where a local set of x , y , and z axes are used, with the origin on a chromium atom and axes toward the octahedral oxygen atoms, the apical oxygen defining the local z axis. It is well-known that the crystal field caused by an octahedron of surrounding negative charges splits the d states of a transition-metal ion, with the three t_{2g} states (d_{xy} , d_{yz} , and d_{zx}) lying lower and the two e_g states ($d_{x^2-y^2}$ and $d_{3z^2-r^2}$) lying higher. Figure 3(b) shows that the d_{xz} , or equivalently, the d_{yz} component of $s(\vec{r})$ is also present, with about half the strength of the d_{xy} component. The e_g states make no noticeable contribution.

Bonding in CrO₂ was analyzed by Sorantin and Schwarz²⁵ and by Burdette *et al.*²⁶ Referring to the DOS in Fig. 2, the sharp band at about -17 eV arises from the oxy-

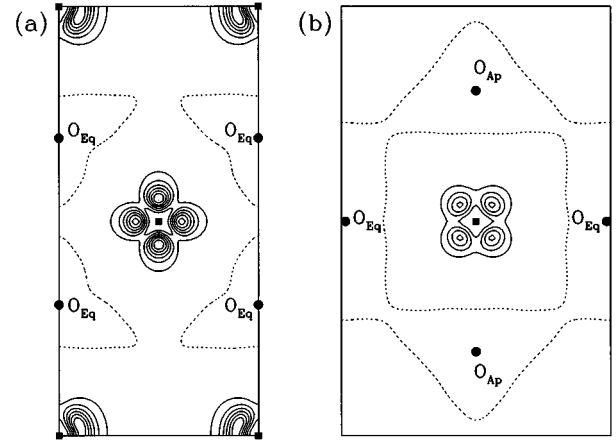


FIG. 3. Spin density of CrO₂ in (a) the equatorial plane of the oxygen octahedron and (b) a plane of the octahedron containing two apical and two equatorial oxygens. Adjacent contour levels are separated by $30\mu_B/\text{unit cell}$, with the zero contour designated by dashed lines. Chromium and oxygen atomic positions are designated by filled squares and circles, respectively. Apical and equatorial oxygen atoms are distinguished by labels.

gen 2s level, and is identical for both spin species, contributing nothing to the spin density. Similarly, the broad band from -7 to -1 eV comes mostly from the oxygen 2p states, with a small admixture of chromium 3d character, and is almost identical for majority and minority spins. The source of the spin density is an exchange splitting of approximately 1.8 eV of the broadbands near and above the Fermi level. These bands are primarily chromium 3d states of t_{2g} parentage, with the e_g bands higher in energy by the crystal-field splitting of approximately 2.5 eV. The exchange splitting shifts the minority-spin d bands above the Fermi level. The majority t_{2g} band is two-thirds filled, with the Fermi level lying in a ‘‘pseudogap’’ in the t_{2g} manifold. Following Sorantin and Schwarz, we can explain the stability and the shape of the spin density in CrO₂ as follows. Only one of the three t_{2g} states participates in covalent oxygen- p -chromium- d hybridization. Hybridization creates both bonding and antibonding hybrid orbitals, with the bonding orbital reduced in energy, appearing in the occupied region of nominally oxygen p states, and the antibonding hybrid orbital remaining in the chromium t_{2g} manifold, but pushed up in energy relative to the two nonbonding members, leaving the ‘‘pseudogap.’’ To see which t_{2g} state hybridizes, consider an oxygen atom with its three coplanar chromium nearest neighbors. This Cr₃O cluster builds σ bonds from hybrids between the two Cr e_g states and two of the three O p states. (This hybridization leaves antibonding e_g states raised in energy relative to t_{2g} states, and is part of the explanation of the crystal-field splitting.) The leftover O p state is the one which points perpendicular to the Cr₃O plane. This state hybridizes by forming a π bond with the Cr t_{2g} state which is correctly oriented. This state is orthogonal to the d_{xy} state which lies in the equatorial plane. Thus one half of the d_{yz} and d_{zx} components of the t_{2g} manifold is pushed upward by antibonding, and this explains the dominance of d_{xy} character in the spin density.

For comparison purposes, we have also computed the

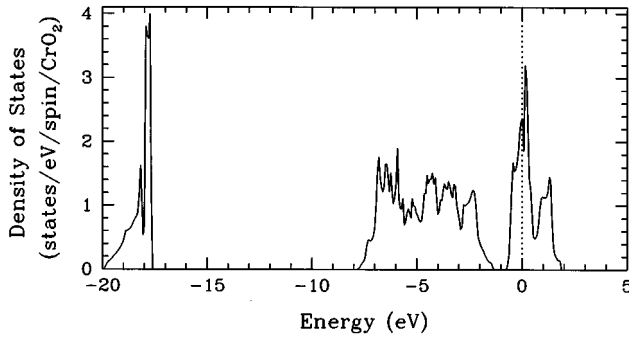


FIG. 4. Density of states for paramagnetic CrO_2 . The dotted line denotes the Fermi energy.

band structure for CrO_2 without spin polarization. The DOS for paramagnetic CrO_2 is plotted in Fig. 4. It agrees fairly well with the linear-muffin-tin-orbital calculation of Kulatov and Mazin,⁷ although they did not find a pseudogap in the chromium t_{2g} band. Note that the Fermi level intersects a sharp peak of the DOS. The large DOS at the Fermi level (2.35 states/eV/ CrO_2 /spin) is an unstable, high-energy situation, which is relieved by the formation of a ferromagnetic phase, according to the usual Stoner argument. The paramagnetic band structure also provides a useful comparison for understanding the electronic transport properties of CrO_2 , as is discussed below.

IV. RAMAN MODE

A symmetry analysis of the zone-center phonons of the rutile structure (space group $P4_2/mnm$) shows that there are four Raman frequencies and four infrared-active (IR) frequencies. The Raman frequencies belong to irreducible representations A_{1g} , A_{2g} , A_{3g} , and E_g , whereas one of the IR frequencies has A_{4u} symmetry, with the rest having E_u symmetry.

The A_{1g} Raman mode is particularly simple, corresponding to fluctuations of the internal coordinate u . Thus the energy of this mode is a by-product of a calculation of the equilibrium structure. Figure 5 shows the variation of the total energy of the crystal as a function of u , for fixed values of the lattice constants a and c . The solid line passing through the data points is a cubic-polynomial fit to the data, with the zero of energy placed at the minimum. As mentioned above, the equilibrium value of u is predicted to be 0.3043. From the curvature of this function at the minimum, we predict the frequency of the A_{1g} Raman mode to be 587 cm^{-1} . To our knowledge, this quantity has not yet been measured.

V. SPECIFIC HEAT

The low-temperature specific heat $C = \gamma T$ was measured²⁷ as $\gamma = 7 \text{ mJ K}^{-2}$ per mole CrO_2 . Using independent-electron theory, $\gamma = (\pi^2 k_B^2/3) N_\gamma(0)$, this corresponds to an effective density of states at the Fermi level of $N_\gamma(0) = 3.0$ states/eV per CrO_2 formula unit. This exceeds our calculated $N(0) = 0.69$ by a factor $1 + \lambda_\gamma = 4.3$, a large enhancement. Conventional metals have an enhancement $1 + \lambda$ from electron-phonon interactions, and it would be possible to

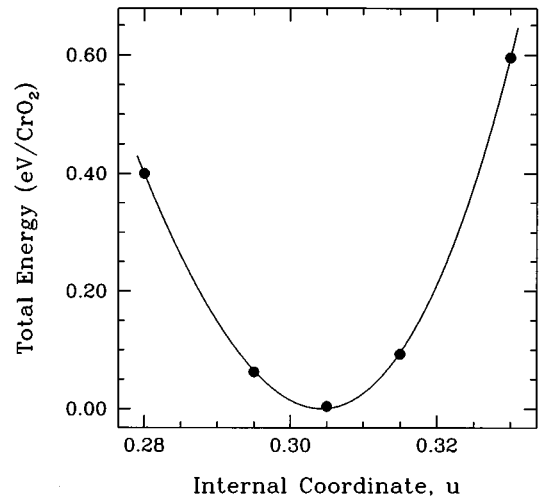


FIG. 5. Total energy vs internal coordinate u for fixed values of lattice parameters a and c .

have λ from this source be fairly large, perhaps as large as 1, but not as large as 3.3. In addition to having the electron-phonon enhancement, ferromagnetic metals can have a mass enhancement from virtual exchange of spin fluctuations. Because of the absence of single-particle states of opposite spin at the Fermi energy, this source is expected to be altered in a half-metallic material.²⁸ Perhaps one could patch up band theory in some way, improving the LSDA exchange-correlation potentials or making self-interaction or gradient corrections, to diminish the enhancement to a more reasonable value. However, given the reasonable success of LSDA in describing the total energy and qualitative nature of the spectrum of electronic excitations farther away from the Fermi surface, it seems to us more likely that the large specific-heat enhancement indicates a correlation effect beyond the reach of a patched-up density-functional theory. Very similar enhancements have been reported in the ferromagnet SrRuO_3 (Ref. 29) and in Sr_2RuO_4 .³⁰

VI. RESISTIVITY

Transport properties of ferromagnets were reviewed by Campbell and Fert.³¹ The electrical resistivity of single-crystal samples of CrO_2 was measured by Redbell, Lommel, and DeVries;³² the data are transcribed in Fig. 6. Similar results were reported by Chamberland.³³ The solid curves in Fig. 6 are Bloch-Grüneisen fits to the low-temperature data.

In order to interpret the resistivity curves, it is useful to choose Ni and Nb as reference materials exhibiting canonical resistivity behavior. The data, shown in Fig. 7, are from Refs. 34–37 for Ni and from Ref. 38 for Nb. Boltzmann transport theory evaluates the current by summing up the velocity of the occupied quasiparticle states. Rather than solving the Boltzmann equation for the quasiparticle distribution function, it is usually a reasonable approximation to use the ansatz that the distribution function F is a displaced Fermi-Dirac distribution, $F_s(\vec{k}) = f(\epsilon_s(\vec{k}) + e\vec{E}\tau_s/\hbar)$. The spin state is labeled by $s = \uparrow$ or \downarrow . This yields a formula for the conductivity,

$$\sigma_{xx} = e^2 N_\uparrow(0) \langle v_{x\uparrow}^2 \rangle \tau_{xx\uparrow} + e^2 N_\downarrow(0) \langle v_{x\downarrow}^2 \rangle \tau_{xx\downarrow}, \quad (1)$$

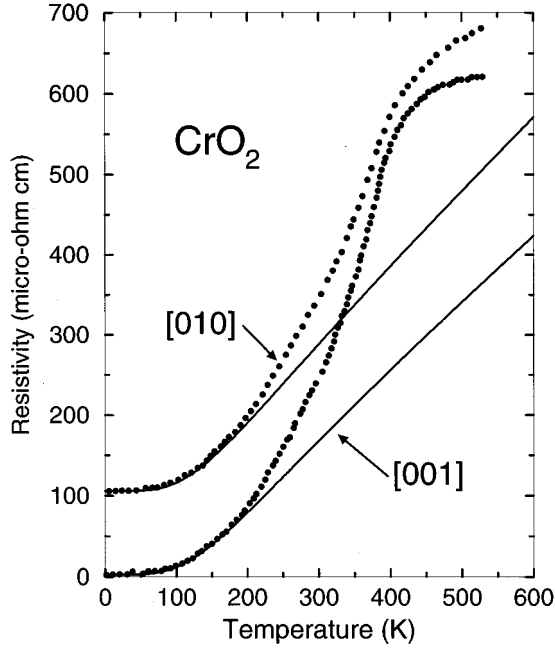


FIG. 6. Measured resistivity of CrO₂ vs temperature from Ref. 32. The data for the [010] direction have been shifted up by 100 $\mu\Omega$ cm for clarity. The solid curves are Bloch-Grüneisen functions fitted to the low- T data, as explained in the text.

where the angular brackets signify a Fermi surface average, $\langle g \rangle \equiv \sum_k g(k) \delta(\epsilon_k) / \sum_k \delta(\epsilon_k)$. The temperature dependence of the resistivity is controlled by the scattering times $\tau_{\alpha\beta s}$. For electron-phonon scattering, this can be modeled by the Bloch-Grüneisen formula

$$\hbar / \tau_{xxs} = 4\pi k_B T \int_0^{\omega_D} \frac{d\Omega}{\Omega} \alpha_{xxs}^2 F(\Omega) \left[\frac{\hbar \Omega / 2k_B T}{\sinh(\hbar \Omega / 2k_B T)} \right]^2, \quad (2)$$

where the Debye model $\alpha_{xxs}^2 F(\Omega) = 2\lambda_{xxs} (\Omega / \omega_D)^4$ is used. If the quasiparticle properties $N_s(0)$ and $\langle v_{xs}^2 \rangle$ are known, then the parameters needed to fit the data are λ_{xxs} and $\Theta_D = \hbar \omega_D / k_B$.

The simplest case to model is Nb, a cubic paramagnet, so that all Cartesian directions and both spin directions have the same value of λ_{xxs} , denoted λ_{tr} . It is convenient to define a ‘‘Drude plasma frequency’’ tensor Ω_P by

$$\Omega_{Pxx}^2 = 4\pi e^2 \sum_s N_s(0) \langle v_{xs}^2 \rangle. \quad (3)$$

Using $\hbar \Omega_P = 9.12$ eV for Nb as calculated by Papaconstantopoulos,³⁹ $\Theta_D = 275$ K from the low- T specific heat,⁴⁰ and setting λ_{tr} equal to the superconducting $\lambda = 1.05$ found in tunneling,⁴¹ the Bloch-Grüneisen curve shown in Fig. 7 follows with no adjustable parameters. A slightly better fit could be produced by reducing the value of Θ_D , which would accord with knowledge from tunneling about the actual effective phonon frequencies. The fit is good up to 500 K, beyond which the data slowly turn downward below the theory, probably signaling the onset of ‘‘saturation.’’⁴² In many elemental d -band metals and intermetallic compounds, when the electron mean free path ℓ becomes less than 10 Å, the thermal increase of resistivity is slowed. When the mean

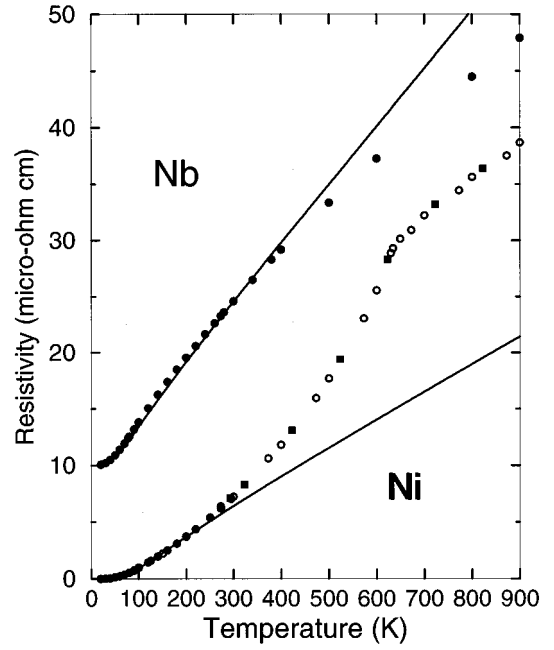


FIG. 7. Resistivity of Ni and Nb vs temperature showing canonical behavior of ferromagnetic and nonmagnetic metals. The data for Ni are from Refs. 34 (filled circles), 35 (open circles), 36 (filled squares), and 37 (open squares). The data for Nb, from Ref. 38, have been shifted up by 10 $\mu\Omega$ cm for clarity. The solid curves are Bloch-Grüneisen functions, as explained in the text.

free path would hypothetically (according to Boltzmann theory) become as short as 5 Å, the temperature dependence is almost completely arrested. Boltzmann theory is expected to fail when ℓ is not large compared with a lattice spacing. Typically this occurs when the resistivity is within a factor of 2 of 100 $\mu\Omega$ cm. From the known parameters of Nb, it is predicted that ℓ (defined as $\langle |\vec{v}|^2 \rangle^{1/2} \tau$) at 500 K should be 14.5 Å, close to (but a little higher than) where ‘‘saturation’’ is expected.

An objection to the procedure used here is that Boltzmann theory needs the velocities of the band quasiparticles, while the single-particle energies ϵ_k calculated using LSDA band theory are not guaranteed to have any physical meaning. The only reliable test of this objection is comparison of LSDA eigenenergies with experimental quasiparticle properties. Tests for the resistivity of paramagnetic metals have generally worked very well,⁴³ similar to the result seen here in Nb.

Nickel is a cubic ferromagnet ($T_{\text{Curie}} = 627$ K), so there are two electron-phonon parameters λ_{\uparrow} and λ_{\downarrow} . The resistivity cannot be fit with Bloch-Grüneisen curves; above 200 K extra scattering occurs because of fluctuating spins. If we assume that below 200 K electron-phonon scattering dominates, we still cannot determine separately all the constants of a Bloch-Grüneisen curve, because at temperatures much less than Θ_D only a single combination $\lambda / \Omega_P^2 \Theta_D^4$ enters the expression. To obtain a rough idea, we make the model $\lambda_{\uparrow} = \lambda_{\downarrow}$ and take $\Theta_D = 450$ K from low- T specific heat. Using the joint up- and down-spin Drude plasma frequency $\Omega_P = 6.96$ eV,³⁹ the Bloch-Grüneisen curve drawn in Fig. 7 corresponds to the choice $\lambda = 0.27$. This is a reasonable value, intermediate between the values 0.13 and 0.47 found for the related metals Cu and Pd,⁴³ and agrees with the result

$\lambda=0.24$ found in the pioneering calculation of Yamashita, Wakoh, and Asano.⁴⁴ It would also be reasonable to choose a lower value of Θ_D , obtaining a correspondingly reduced value of λ , and a fit which follows the experimental $\rho(T)$ up to a somewhat smaller temperature. From the measured specific heat and the band values of Papaconstantopoulos, one finds $\lambda_\gamma \approx 0.70$, significantly larger than can be reconciled with resistivity, and suggesting that there is an additional source of renormalization beyond electron-phonon effects.

In principle, Boltzmann theory should still work for Ni at temperatures up to at least $T=900$ K. If the electron-phonon mechanism alone were causing scattering, then the value $\lambda=0.27$ implies that the mean free path for up-spin electrons would be 35 Å, and for down-spin electrons would be 12 Å, using the Fermi velocities found by Papaconstantopoulos.³⁹ However, the actual resistivities, because of spin scattering, are higher by 1.72 than the electron-phonon fit, so the corresponding mean-free paths are reduced to 20 and 7 Å, respectively. But at 900 K Ni is no longer a ferromagnet, and separate up- and down-spin Fermi surfaces no longer exist. Nevertheless, the mean free paths suggested by this analysis are long enough that it seems likely that the basic premises of Boltzmann theory are not badly violated. The fact that $\rho(T)$ continues to increase with temperature at 900 K suggests a metal where transport is still governed by propagating quasiparticles which scatter more rapidly at higher T .

We now apply this kind of analysis to CrO_2 . At low temperature, there are only majority (up) spins at the Fermi surface, and thus only two electron-phonon parameters λ_{xx} and λ_{zz} , which can be separately fit to ρ_{xx} and ρ_{zz} . The Bloch-Grüneisen curves of Fig. 6 use $\Theta_D=750$ K, taken from low- T specific heat of the neighboring compound TiO_2 .⁴⁵ Using the calculated plasma frequencies tabulated in Table I, we find $\lambda_{xx} \approx 0.8$ and $\lambda_{zz} \approx 0.9$. These values are a little higher than found in typical oxide metals [compare $\lambda \approx 0.45$ in RuO_2 (Ref. 46)]. The values of λ are reduced by a factor of 2 if we fit using $\Theta_D=500$ K, which characterizes the specific heat of TiO_2 in the range 15–65 K,⁴⁵ and is an equally reasonable choice. The corresponding Bloch-Grüneisen curves deviate from the measured $\rho(T)$ at $T > 125$ K instead of the $T > 190$ K seen in Fig. 6. In either case, because of the small Fermi velocities, the corresponding ℓ values become small at higher T .

The mean free path has no unique definition. Previously we used $\ell = \langle |\vec{v}|^2 \rangle^{1/2} \tau$, but an equally good choice is $\ell = \langle |\vec{v}|^2 \rangle \tau / \langle |\vec{v}| \rangle$. In ferromagnetic CrO_2 we find $\langle |\vec{v}|^2 \rangle^{1/2} = 2.5 \times 10^5$ m/s and $\langle |\vec{v}| \rangle = 2.2 \times 10^5$ m/s, so the two definitions differ by an unimportant amount. Boltzmann theory gives the following approximate relation:

$$\ell = \frac{\sum |\vec{v}_k|^2 \tau \delta(\epsilon_k)}{\sum |\vec{v}_k| \delta(\epsilon_k)} \cong \frac{(2\pi)^3 \hbar}{e^2} \frac{1}{A_{\text{FS}}^{\uparrow} + A_{\text{FS}}^{\downarrow}} \left(\frac{1}{\rho_{xx}} + \frac{1}{\rho_{yy}} + \frac{1}{\rho_{zz}} \right). \quad (4)$$

This provides a robust way to estimate mean free paths, because the only theoretical input required is the area A_{FS}^s of

TABLE I. Measured, calculated, and derived properties of CrO_2 .

Quantity	Ferromagnetic	Paramagnetic
Experimental values		
a (Å)	4.419 ^a	
c (Å)	2.912 ^a	
u	0.303 ^a	
Saturation moment μ (μ_B/CrO_2)	2.0 ^b	
γ (mJ/mole K)	7 ^c	
$\rho(0 \text{ K})$ ($\mu\Omega \text{ cm}$)	≈ 5 ^d	
$\rho(300 \text{ K})$	250 ^d	
$\rho(500 \text{ K})$		570 ^d
Theoretical values		
u	0.3043	
μ (μ_B/CrO_2)	2	
$\omega(A_{1g})$ (cm^{-1})	587	
$N(0)$ (states/eV/spin/ CrO_2)	0.69	2.35
$\sqrt{\langle v_{Fx}^2 \rangle}$ (10^5 m/s)	1.38	0.62
$\sqrt{\langle v_{Fz}^2 \rangle}$	1.56	0.79
$\Omega_{p_{xx}}$ (eV)	1.91	2.22
$\Omega_{p_{zz}}$	2.15	2.84
Fermi-surface area (Å^{-2})	8.86	21.43
Derived values		
$1 + \lambda_\gamma = N_\gamma(0)/N(0)$	4.3	
Mean free path $\ell(5 \text{ K})$ (Å)	700	
$\ell(300 \text{ K})$	14	
$\ell(500 \text{ K})$		1.3

^aReference 21.

^bReferences 23 and 24.

^cReference 24.

^dReference 32.

the Fermi surface. Density-functional theory has an excellent ability to give the correct shape of Fermi surfaces, even under conditions where the velocity of the quasiparticles at the Fermi surface, or the density of states, may be off. Our calculated areas are given in Table I. At low T , where ρ is only a few $\mu\Omega \text{ cm}$, ℓ in CrO_2 is hundreds of Å. At $T=200$ K, we estimate $\ell=36$ Å. This is still the regime of a good band Fermi liquid. At higher T , the resistivity increases rapidly, and ℓ diminishes to ≈ 7 Å at the Curie temperature 390 K. This number is estimated assuming the ferromagnetic electronic structure. If instead we use the paramagnetic Fermi surface, the area is much larger and values of ℓ are reduced by a factor of 4.8 to sizes less than 2 Å. This is the regime which has been called a “bad metal” by Kivelson and Emery.⁴⁷ In traditional bad metals, like A15 structure intermetallics (Nb_3Sn , etc.), the resistivity is temperature independent at this point, but in “exotic bad metals” like the high- T_c superconductors, resistivity continues to rise even though propagating quasiparticle states of the Landau type cannot be present. Earlier⁴⁸ we found that the high- T metallic (rutile structure) phase of VO_2 is also a “bad metal” in the “exotic” sense, as is the ferromagnet SrRuO_3 ,²⁹ so it should not be surprising if CrO_2 is as well.

It is interesting to think about the nature of scattering in CrO_2 at temperatures near T_{Curie} . Figure 6 suggests that

roughly half the scattering involves spin flips caused by spin fluctuations. The mean distance between spin-flip scatterings is $\approx \sqrt{2}l$, or 10 Å. A spin flip takes an electron off the majority (up) spin Fermi surface into an insulating gap. It cannot remain there long unless joined by a sufficient number of other flipped electrons such that the local majority has changed spin direction, and the down-spins are now metallic with a Fermi surface, leaving up-spins insulating. Thus it is easy to imagine that the scattering is not completely incoherent, but has a collective feature. As temperature rises to near the Curie temperature, the bulk magnetization decreases primarily through fluctuating formation of opposite spin domains. It seems natural to associate the spin-flip scattering length with the size of these domains. Above T_{Curie} the same picture can be used, except that now the volume fraction of up and down domains is equal. Within each domain, electrons roughly behave as if they had the ferromagnetic band

structure, with majority-spin electrons having a Fermi surface, but badly lifetime broadened. With a 10-Å spin-flip mean free path, and a 7-Å total mean free path, the local Fermi-liquid picture is close to total destruction. Looking at the resistivity shown in Fig. 6, it is hard to tell whether the resistivity is saturating or not. Additional measurements at higher T would be interesting.

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