

Resistivity of the high-temperature metallic phase of VO₂

Philip B. Allen, Renata M. Wentzcovitch,* and Werner W. Schulz

Department of Physics, State University of New York at Stony Brook, Stony Brook, New York 11794-3800

Paul C. Canfield†

Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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Measurements are reported of the electrical resistivity $\rho(T)$ along the c axis of a single crystal of VO₂, from the metal-insulator transition at $T=333$ K up to 840 K. The temperature dependence is very linear, and a fit to Bloch-Grüneisen theory gives a residual resistivity $\rho_0=65 \mu\Omega$ cm and a ratio $\rho(840 \text{ K})/\rho_0=8$. With the help of a local-density-approximation band-structure calculation, we further pursue the conventional (Bloch-Boltzmann) interpretation by extracting the electron-phonon coupling constant $\lambda=1.1$ and the mean free path $\ell(800 \text{ K})=3.3 \text{ \AA}$. The short mean free path implies that the conventional interpretation is internally inconsistent. The most likely explanation is that unknown internal damage (e.g., cracks) has altered the effective cross section of the sample, causing the measured resistivity to be overestimated by a factor ≥ 3 . Another possibility is that, in common with the normal state of copper oxide superconductors, metallic VO₂ may not be a conventional Fermi liquid.

I. INTRODUCTION

Most oxides are not metals, but those which are metallic display diverse behavior,^{1,2} including ordinary Fermi liquids such as ReO₃ (Ref. 3) and NbO,⁴ itinerant ferromagnets such as CrO₂, and high- T_c superconductors. Although the mechanism of superconductivity is still controversial, the most dramatic characteristic which correlates with high T_c is that cuprate superconductors belong to a rare category, doped Mott insulators. This motivates further investigation of other presumed Mott insulators such as V₂O₃.⁵ A very interesting related material is VO₂, which switches from insulating at low T to a good conductor at $T > T_{\text{MI}}=333$ K (where MI denotes metal insulator). The conductivity jump, up to 10^5 in good samples, is one of the most dramatic temperature-driven conductivity changes known. Whether the insulating phase should be called a Mott insulator is a matter of debate.⁶ Unlike most other candidate Mott insulators, there is no sign⁷ of antiferromagnetic order. Instead there is a cell-doubling structural phase transition with a small change in volume but significant internal atomic rearrangement crudely characterized as a dimerization of vanadium atoms along the c axis.⁸ Although symmetry would permit the transition to be second order, experiment shows it is first order, with some evidence for precursors in the metallic phase.^{8,9} Model calculations by Gervais and Kress¹⁰ indicate a possible soft zone-boundary phonon. A Peierls-type electron-phonon mechanism, involving delicate k -space nesting, does not seem likely, because samples so highly disordered as to be scarcely crystalline have a conductivity jump of 10^3 at a temperature hardly shifted from 333 K.¹¹ Therefore one might characterize the ground state as a “bipolaronic crystal,” reminiscent of BaBiO₃. Views which permit both correlations and distortions to play a role

are the valence bond picture as supported by Heitler-London theory by Sommers and Doniach,¹² and the “spin Peierls” scenario, as advocated by Shi, Bruinsma, and Bishop.¹³ The simultaneous similarities and diversities of metal-insulator transitions in vanadium oxides defy classification by simple categories and suggest that no single model correctly captures all the relevant physics.

Not very much is known about the physical properties of the high- T metallic phase, which has the undistorted rutile structure in common with a number of other metallic oxides which are often good conductors. This motivates us to study the electrical resistivity.

II. EXPERIMENT

The single crystals of VO₂ were grown out of a V₂O₅ flux by a method similar to that described for intermetallics.¹⁴ The crystals grown by this method are needlelike, elongated along the c axis of the nearly tetragonal unit cell. The needles tend to be fibrous, with nonuniform cross sections. In addition, as VO₂ is cooled through the MI transition, it has a tendency to crack or shatter with the strain of the structural distortion. In many samples this leads to a large residual resistivity term and “nonmetallic” temperature dependence of resistivity in the metallic phase. Generally, the crystals with the cleanest morphology (no evident twinning, etc.) are the ones more likely to cycle through the MI transition undamaged.

The ac resistivity was measured with the current flowing along the c axis using a lock-in amplifier by a conventional four-probe technique. The sample dimensions were $\ell \times w \times t$, with $\ell(\parallel c) = 1.40 \pm 0.02$ mm and $w \sim t = 0.18 \pm 0.01$ mm. Berglund and Guggenheim¹⁵ reported a sample with a conductivity jump of $\sim 10^5$ and a temperature derivative $d\rho/dT$ in the normal state five

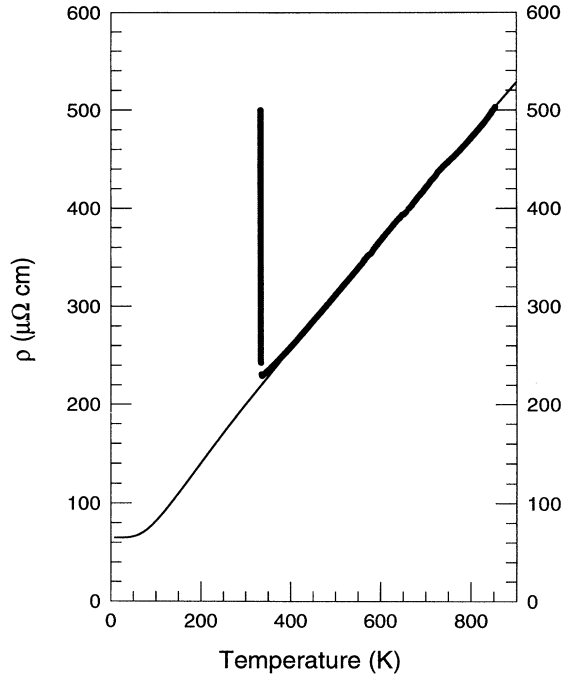


FIG. 1. Temperature dependence of the resistivity of VO_2 . The thin line is the Bloch-Grüneisen fit.

times smaller than our value. A possible resolution of the discrepancy is to assume that the effective cross section of our sample was smaller than we measured by a factor of 5, owing to damage such as cracks which remove parts of the sample from the current path. Since the ratio of our sample resistance at $T = 500$ K to the sample resistance at $T = 350$ K is actually better than that found in Ref. 15, we do not think that the high resistivity is due to impurities.

The data are shown in Fig. 1, with a Bloch-Grüneisen fit which extrapolates the metallic data down through the insulating range to $T=0$. This fit is discussed in the next section.

III. THEORY

We have used self-consistent local-density-approximation (LDA) band theory and Troullier-Martins¹⁶ soft separable pseudopotentials to calculate the energy bands and total energy of VO_2 . The Perdew-Zunger¹⁷ parametrization of the Ceperley-Alder¹⁸ exchange-correlation function was used. The plane-wave basis set was expanded up to an energy cutoff of 64 Ry. Charge densities were constructed using six k points in the irreducible Brillouin zone and an electronic Fermi occupancy temperature of 340 K. Electronic eigenvalues were stable to better than 0.1 eV when the mesh was increased to 18 k points or when the occupancy temperature was changed. The high-temperature tetragonal rutile-structure phase was computed at several lattice constants in the range of the experimental values. The parameters used in our final calculations are

TABLE I. Results of LDA band calculation, and results of fitting data of Fig. 1. The rms Fermi velocity includes all three Cartesian components, and was used to calculate the mean free path ℓ .

Calculated properties	
$N(0)$ (states/eV f.u.) (both spins)	4.18
$\sqrt{\langle v_F^2 \rangle}$ (m/sec)	0.24×10^6
Ω_{paa} (eV)	5.4
Ω_{pcc} (eV)	2.9
Fitted properties	
ρ_0 ($\mu\Omega$ cm)	65
λ_{cc}	1.1
ℓ (\AA) (at 800 K)	3.3

$a = 4.555$ \AA , $c = 2.851$ \AA , and the internal coordinate $u = 0.300$. These were measured⁸ at 360 K. When the slightly different coordinates measured at 473 K were used, the changes were insignificant. However, when the presumably less accurate parameters of Westman¹⁹ ($a = 4.530$ \AA , $c = 2.869$ \AA , and $u = 0.305$) were used, the nonbonding d bands at the Fermi level narrowed slightly, and the next highest band, an antibonding vanadium- d /oxygen- p (π^*) level, shifts by a few tenths of a volt, causing a significant change of shape of the Fermi surface and a noticeable alteration of the density of states and effective masses. Our results, shown in Table I and Fig. 2,

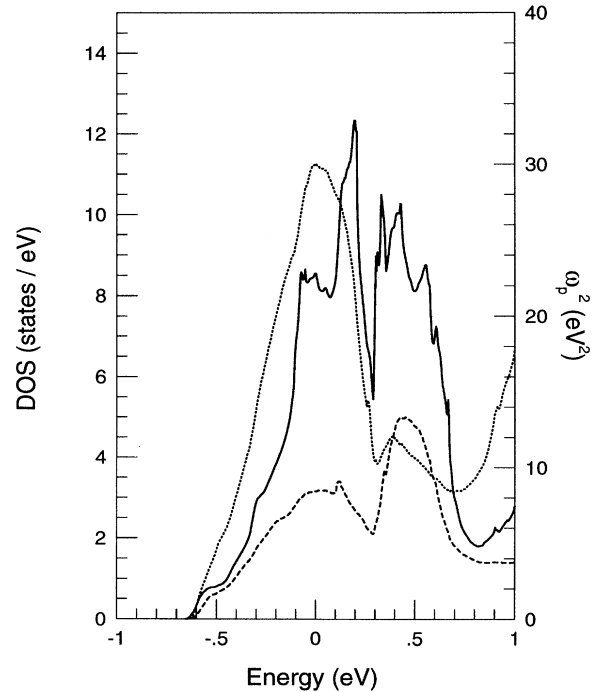


FIG. 2. Density of states (solid line, left-hand scale) of rutile-structure VO_2 (units are states of both spin per eV per formula unit) vs energy for a narrow range near the Fermi level at $E = 0$. Also shown are Ω_{aa}^2 (dotted line) and Ω_{cc}^2 (dashed line) on the right-hand scale. One electron per V atom is in the nonbonding d -type band shown. Twelve electrons per VO_2 are in bands of primarily oxygen p character which lie in the range between -8 and -2 eV.

bear a qualitative resemblance to the non-self-consistent calculations of Caruthers, Kleinmann, and Zhang²⁰ and Gupta, Freeman, and Ellis.²¹ Details of Fermi-surface geometry and density of states near the Fermi energy are significantly altered, both by the self-consistent nature of our calculation and by the fact that these previous calculations used the lattice parameters of Ref. 19.

A. Susceptibility

The magnetic susceptibility of the metallic phase of VO₂ is 6.7×10^{-4} emu/mole,²² which is high for a paramagnetic metal [pure V (Ref. 23) has $\chi = 2.9 \times 10^{-4}$ emu/mole]. The susceptibility of metallic VO₂ has a greater T dependence than in ordinary metals such as V, but not greater than what is seen at high T in V₃Si.²⁴ Our calculated density of states at the Fermi level $N(0)=4.18$ (states/eV formula unit) is high and yields a noninteracting spin susceptibility $\chi_{\text{spin}}^0 = \mu_B^2 N(0) = 1.35 \times 10^{-4}$ emu/mole, five times smaller than the measured χ . A similar ratio occurs in elemental V, where $N(0)=1.64$ states/eV yields $\chi_{\text{spin}}^0 = 0.53 \times 10^{-4}$ emu/mole, 5.5 times smaller than experiment. It is difficult to be sure how much of the measured susceptibility is caused by orbital rather than spin effects, but in V the orbital part is claimed to be 50% or higher.²³ The Stoner enhancement of the spin susceptibility of V was calculated by Janak²⁵ to be 2.3. Since there is little doubt that elemental V is an ordinary Fermi liquid, by comparison it is at least plausible to reconcile the large susceptibility of VO₂ with the band Fermi-liquid model by incorporating exchange enhancement and orbital contributions.

B. Resistivity

For purposes of analyzing resistivity, the Drude plasma frequency tensor components $\Omega_{p\alpha\alpha}$ were computed, as well as the density of states $N(0)$ at the Fermi surface and the mean-square Fermi velocities $\langle v^2 \rangle$. Brillouin-zone integrations used LDA energies calculated at 112 \mathbf{k} points to generate a Fourier interpolation, followed by linear (tetrahedron) interpolation. Four bands of primarily vanadium d character intersect the Fermi level. The results are given in Fig. 2 and Table I. Our results should probably not be compared closely with the optically measured Drude plasma frequencies of Verleur, Barker, and Berglund,²⁶ who fitted $\Omega_{pcc}=4.2$ eV and $\Omega_{paa}=3.56$ eV to $\epsilon_{2\alpha\alpha}(\omega)$ extracted from reflectivity data from 0.2 to 4.5 eV. Although the orders of magnitude agree with our calculation, the anisotropy is reversed. It is rare for a metal to have such a benign optical spectrum that a reliable dc Drude plasma frequency can be extracted. Almost inevitably there are interband transitions in $\epsilon_2(\omega)$ in the range of ω needed to make the fit. For VO₂ with four narrow bands intersecting the Fermi level, this problem is especially severe. A sign that the measured Drude plasma frequencies are contaminated by interband effects is the very large Drude damping rate $1/\tau \approx 1.2$ eV, fitted

in Ref. 26, much larger than the one which enters the dc resistivity.

The resistivity of a normal Fermi liquid is described by the Bloch-Boltzmann equation.²⁷ An accurate variational solution of this equation^{28,29} yields

$$\rho_{\alpha\alpha} = 4\pi/\Omega_{p\alpha\alpha}^2 \tau_{\alpha\alpha}, \quad (1)$$

$$\Omega_{p\alpha\alpha}^2 = 4\pi e^2 \sum_k v_{k\alpha}^2 \delta(\epsilon_k), \quad (2)$$

$$1/\tau_{\alpha\alpha} = 1/\tau_{\alpha\alpha}^{imp} + 1/\tau_{\alpha\alpha}^{ep} + \dots \quad (3)$$

Here $k = (\mathbf{k}n)$ (wave vector and band index), $\hbar v_{k\alpha} = \partial\epsilon/\partial k_\alpha$ is the band velocity, and Ω_p is the Drude plasma frequency. Closed-form expressions for $1/\tau$ can be given in terms of the electron-impurity and electron-phonon matrix elements, the phonon frequencies and polarization vectors, and double averages over all initial and final states on the Fermi surface.²⁸ Because phonons are not known for VO₂ it is necessary to introduce phenomenological parameters. The simplest model is Bloch-Grüneisen theory,²⁷ involving the residual resistivity ρ_0 , the Debye temperature Θ_D , and the electron-phonon coupling constant λ :

$$\hbar/\tau_{\alpha\alpha}^{ep} = 2\pi\lambda_{\alpha\alpha} k_B T f_{BG}(T/\Theta_D), \quad (4)$$

$$f_{BG}(T/\Theta_D) = 4(2T/\Theta_D)^4 \int_0^{\Theta_D/2T} dx x^5 / \sinh^2(x). \quad (5)$$

The function f_{BG} has the low- T limit $497.7(T/\Theta_D)^4$, and the high- T limit $1 - \Theta_D^2/18T^2 + \dots$. The complete variational solution has a similar form, with the same coupling constant $\lambda_{\alpha\alpha}$ and a temperature dependence which has the same limits as f_{BG} except that the low- T Debye temperature and the high- T Debye temperature are no longer the same. The electron-phonon coupling constants $\lambda_{\alpha\alpha}$ are only weakly dependent on Cartesian direction α for noncubic metals³⁰ and agree closely (typically $\approx 10\%$) with the superconducting λ .²⁹ Empirical parameters ρ_0 and λ_{cc} are shown in Table I. A value $\lambda=1.1$ is characteristic of a good superconducting element such as Nb or a fairly high- T_c compound such as NbC. Most oxide metals such as ReO₃ and RuO₂ probably have values $\lambda \leq 0.3$, but the occurrence of superconductivity in LiTi₂O₄ at 12 K (Ref. 31) shows that $\lambda \approx 1$ would not be unique for a transition-metal oxide. Because of the absence of metallic resistivity below 333 K, our fit is not sensitive to the choice of Θ_D . A reasonable value $\Theta_D=500$ K was chosen arbitrarily. Our band calculations permit us to predict that the ratio of resistivities ρ_{aa}/ρ_{cc} should be $\Omega_{pcc}^2/\Omega_{paa}^2=0.29$, and only weakly T dependent above T_{MI} . Sample morphology has so far prevented us testing this prediction. Two previously published values of resistivity anisotropy are $\rho_{aa}/\rho_{cc} \sim 0.6 - 0.7$ from Kosuge⁷ and ~ 0.4 from Bongers.³² The latter value was obtained on a sample with a metallic resistivity as low as 200 $\mu\Omega$ cm and a resistivity jump of $\sim 10^5$, whereas the sample of Kosuge showed a resistivity discontinuity of only a factor of 10^2 , and a “metallic” resistivity $\geq 3 \Omega$ cm, larger

than ours by 10^4 . Thus we favor the value of Bongers, which agrees adequately with the band prediction.

An important consistency test is that the mean free path $\ell = \sqrt{\langle v_k^2 \rangle} \tau$ should be long enough that electrons can be assigned a propagation vector; that is, $k\ell \gg 1$ is required for the validity of the Boltzmann equation. In the case of elements it has been observed³⁰ that as long as $\ell > 10 \text{ \AA}$, departures from Boltzmann behavior are too weak to see by eye in the data, whereas when $\ell < 10 \text{ \AA}$, the characteristic "saturation" behavior³³ occurs. Table I also shows the estimated value $\ell \approx 3 \text{ \AA}$ at 800 K. Since saturation is not occurring in the data of Fig. 1, we conclude that our Bloch-Boltzmann analysis is internally inconsistent. The first explanation that comes to mind is a possible inadequacy of the band structure. This seems unlikely to us, because usually band theory is very reliable for metals, except possibly for a scale change taking $(\epsilon_k - \epsilon_F)$ into $(\epsilon_k - \epsilon_F)/(1 + \alpha)$. For example, in UPt_3 , the shape of the Fermi surface was correctly predicted,³⁴⁻³⁶ even though a renormalization $1 + \alpha \approx 20$ was necessary to agree with the density of states seen in the heat capacity. For nonmagnetic metallic elements, comparison between superconductivity and resistivity³⁰ has shown no need for any renormalization. But if a renormalization were needed for VO_2 , this would take velocities into $v_k/(1 + \alpha)$, density of states into $N(0)(1 + \alpha)$, and Drude plasma frequency squared into $\Omega_p^2/(1 + \alpha)$. Therefore the empirical λ_{cc} would become $\lambda_{cc}/(1 + \alpha)$, and the resulting estimated mean free path, being the ratio of v_F to λ_{cc} , would be unaffected. It is not possible to lengthen ℓ by rescaling the band structure.

Two other possible explanations come to mind. The likely one is that the magnitude of the measured resistivity is too large by a factor of at least 3 (earlier we indicated a possible factor of 5 by comparison with the data of Ref. 15). This would reduce λ_{cc} and enhance ℓ

by the same factor of at least 3. The reason why the magnitude of ρ may be overestimated is that undetected internal flaws like cracks can reduce the effective sample cross sectional area. Since cracking often happens when the sample is heated through T_{MI} , this seems a very real possibility. A more interesting possible explanation is that VO_2 , like the copper oxide superconductors, might not be a conventional Fermi liquid. The same difficulty of dangerously short mean free paths arises when band theory is used to analyze $\rho(T)$ in these materials.³⁷

IV. SUGGESTIONS

Further studies of VO_2 would be interesting. Problems of cracking might be avoided in thin-film samples on an appropriate substrate, or if measured *in situ* before the sample is ever cooled through T_{MI} . Since band theory³⁸ indicates that the rutile phase is metastable at $T=0$, it might be possible to stabilize this phase at $T < T_{MI}$ by epitaxial growth on a lattice-matched substrate.

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* Present address: Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom.

[†] Present address: Ames Laboratory, Condensed Matter Physics Division, Ames, IA 50011.

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