# Piezoresistivity and the semiconductor-semimetal transition in Ti<sub>2</sub>O<sub>3</sub>

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We have measured the effect of stress on the electrical resistivity of single-crystal  $Ti_2O_3$  using hydrostatic pressure between 270 and 400 K and uniaxial compression between 296 and 500 K in order to study the semiconductor-semimetal transition in this material. Large fractional changes in resistivity per unit stress (piezoresistivities) were found. They are explained as a consequence of Fermi-level motion due to strain changing the gap, or overlap, between conduction and valence bands and thereby the concentration of mobile charge carriers. Extrema in the piezoresistivities, observed near 460 K using uniaxial compression, result from the temperature dependences of the elastic compliances. Simple approximate expressions for the piezoresistivity of statistically degenerate charge carriers scattered by polar optical-mode phonons are compared with our data above 460 K. This yields deformation potentials for the relative motion of the valence and conduction bands whose values are consistent with those deduced from the piezoresistivity of semiconducting  $Ti_2O_3$  and from elastic-constant data through the transition. The amount of band overlap is much smaller than that used previously to account for elastic constant and specific heat "anomalies" in the temperature range of the semimetal-semiconductor transition, but is consistent with recent reflectance results and analyses of lattice parameter and elastic-constant data.

#### I. INTRODUCTION

The semiconductor-semimetal (SC-SM) transition in  $Ti_2O_3$  between 400 and 500 K has been the subject of a number of investigations.<sup>1</sup> The approach and overlap<sup>2</sup> of a Ti 3*d* valence band (comprised of  $a_{1s}$ -like orbitals) and a conduction band (comprised of  $e_s^{\pi}$ -like orbitals) has been able to account, at least qualitatively, for the behavior of the electrical conductivity,<sup>3</sup> a heat-capacity maximum,<sup>4</sup> anomalies in the elastic constants,<sup>5</sup> and the shift in frequency of the lowest-lying Raman mode.<sup>6</sup> Large changes in the lattice parameters<sup>7</sup> and a maximum in the ultrasonic attenuation<sup>8</sup> are associated with the transition, but these phenomena have not been explained very well yet.

The most comprehensive model of the transition involves a free-energy calculation<sup>9</sup> which includes electron-electron Coulomb energy, elastic energy, and band electron entropy for admittedly simplified  $a_{1s}$ -like and  $e_s^{\pi}$ -like Ti 3d bands whose edges approach and cross with increasing temperature. Various properties calculated for Ti<sub>2</sub>O<sub>3</sub> using this model<sup>9</sup> are in qualitative agreement with experimental results. However, the calculated magnetic susceptibility disagrees badly with that measured.<sup>10</sup> The values of the forbidden band gap at zero temperature, bandwidths, and deformation-potential parameter in this model are much smaller than those deduced from experiment.<sup>4,5,11</sup> For a discussion of these features, see Ref. 9.

A band-structure calculation<sup>12</sup> has been made for  $Ti_2O_3$  at T=0 K, but it failed to yield a forbidden energy gap. The authors did show how the effect of Coulomb interactions between electrons might open up a gap but did not recalculate the band structure using them. It has also been suggested<sup>13</sup> that the formation of a nondegenerate gas of conduction-band polarons must be involved in the electrical transition. However, recently<sup>14</sup> the static and optical dielectric constants and their difference have been found to be so large ( $\overline{K}_0 = 45$ and  $\overline{K}_\infty = 29.5$ ) that the polaron binding energy would have a much smaller value than had been estimated previously.<sup>13</sup>

In view of the limited success of theoretical models in explaining various properties of  $Ti_2O_3$ in the region of the electrical transition and the usefulness of piezoresistance measurements<sup>15</sup> for studying electronic band structure and scattering processes, we began investigating the effect of stress on the resistivity of  $Ti_2O_3$ . Information obtained thereby about band structure and deformation potentials in the temperature region where  $Ti_2O_3$  is semiconducting has been published recently.<sup>16</sup> In this paper we shall present piezoresistivity (fractional change of resistivity per unit stress) results between 270 and 500 K.

## **II. EXPERIMENTAL DETAILS**

Our experimental procedures are like those discussed elsewhere<sup>16</sup> except that in the present work electrical contacts were made with an alloy of 97% In and 3% Sb, instead of with indium, and the sample system and a heater coil were immersed in a bath of Dow Corning 200 fluid. The bath temperature was controlled by a Fisher proportional temperature control to within  $\pm 0.08$  K or better. Uniaxial compressions up to  $2 \times 10^8$  dyn/cm<sup>2</sup> and hy-

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drostatic pressures up to  $3 \times 10^9$  dyn/cm<sup>2</sup> were used producing, respectively, maximum percentage changes in resistivity ranging from 0.2% to 5% and from 2% to 5%.

We measured change in sample voltage due to stress at constant current. This yielded change in resistance which we corrected for dimensional changes to obtain change in resistivity. In the case of uniaxial stress, the resistance change might not have been isothermal. We estimate that even if the stress application had been completely adiabatic, only a very small correction<sup>15</sup> to the data would be necessary to obtain isothermal values. The error in our piezoresistivity values was 10% or less.

### **III. RESULTS**

Figure 1 summarizes our uniaxial compression data. It can be seen that the piezoresistivity exhibits an extremum in each of three major crystallographic directions of this  $\alpha$ -corundum-type structure. Since the piezoresistivity depends on the values of the elastic-compliance constants  $(S_{ij}$ 's), it is pertinent to consider what influence they might have on the piezoresistivities because the elastic-stiffness constants  $(C_{ij}$ 's) are known to exhibit anomalies<sup>5</sup> in the region of the electrical transition. Using the pertinent experimental values of the  $C_{ij}$ 's we calculated the appropriate  $S_{ij}$ 's. Then we formed the combinations of them



FIG. 1. Piezoresistivity vs temperature for uniaxial compression  $\vec{X}$ , sample length, and current  $\vec{I}$ , parallel to the *c* axis, the *a* axis, and a direction  $\vec{d}$ , which is 45° from  $\vec{c}$  and 90° from  $\vec{a}$ . Small symbols indicate data and large symbols indicate calculated values. (The curves are drawn through the data to aid the eye.)



FIG. 2. Linear combinations of isothermal elastic compliances which would be proportional to strain-induced shifts in the relative positions of the valence and conduction bands if  $-A_3=A_1>0$ , where  $A_1$  and  $A_3$  are deformation potentials parallel to the *a* axis and to the *c* axis, respectively.

which would be proportional to the strain induced separations between valence and conduction bands<sup>16</sup> if the deformation potentials parallel and perpendicular to the c axis,  $A_3$  and  $A_1$ , respectively, were equal in magnitude and opposite in sign and  $A_3$  is negative. The results shown in Fig. 2, indicate that each  $S_{ij}$  combination exhibits an extremum which is similar in shape but much smaller in magnitude than the piezoresistivity measured for that direction.

In Fig. 3 we show the effects of hydrostatic pressure on the resistivity between 275 and 400 K. It can be seen that the piezoresistivity becomes ever more negative with increasing T in this range. Unfortunately, we could not make measurements at higher temperatures to look for extrema like those we found with uniaxial compression. However, work of others<sup>17</sup> implies that the hydrostatic piezoresistivity has a sharp minimum between 400 and 500 K. (These authors<sup>17</sup> found the magnitude of the hydrostatic piezoresistivity to be much larger than we did at the same temperatures and pressures. We do not know the reason for the discrepancy. It may be due to the poor accuracy of their method, making resistivity versus temperature measurements at pressures which were not sufficiently constant. We measured resistivity versus pressure at various carefully controlled temperatures, obtaining pressure values from a precision dial gauge which were confirmed by



FIG. 3. Piezoresistivity due to hydrostatic pressure vs temperature for sample length and current parallel to the same three crystallographic directions as in Fig. 1. Symbols indicate data. (The curves are simply drawn through the data to aid the eye.)

those obtained from a calibrated Manganin cell. We believe our hydrostatic data are correct. They are consistent with our uniaxial results.)

#### IV. DISCUSSION

The piezoresistivities which we have observed with uniaxial compression are too large in magnitude and of opposite sign to those which could arise from the stress causing a temperature shift even if the stress application had been completely adiabatic. The extrema are also too large in magnitude to be due simply to changes in the mobility of charge carriers. Previously,<sup>18,19</sup> we had suggested a mobility explanation which required the (polar) optical phonons which scatter the charge  $\operatorname{carriers}^{20}$ to have anharmonicity parameters, which go through very large extrema as the (SC-SM) transition is traversed. Subsequent infrared reflectance<sup>14,21</sup> measurements have provided no evidence for such phonon anharmonicity. Therefore, we have abandoned this change of mobility explanation for our piezoresistivity extrema. Neither is their any evidence that other parameters such as effective charge, dielectric constant, and the effective mass and screening vector of the charge carriers, have the very large, temperature-dependent sensitivity to stress which would be needed to explain our piezoresistivity results in terms of changes in the scattering provided by polar optical modes.<sup>22,23</sup>

We do suggest that the large piezoresistivities are due to change in the Fermi energy as electrons redistribute themselves between the valence and conduction bands when these bands are shifted relative to each other by stress. The large size and peculiar shapes are due partly to a given stress producing more strain where the elastic constants exhibit anomalies. (Figure 2 illustrates this point.)

A rigorous calculation of the piezoresistivity through our whole experimental temperature range is beyond the scope of the present work because of the difficulties inherent<sup>22,23</sup> in treating polar optical mode scattering, the intermediate amount of statistical degeneracy, and the presence of two conducting bands with a temperature dependent gap or overlap. Nevertheless, for temperatures where the bands are overlapped sufficiently, we feel justified in using the form which the conductivity takes in the degenerate limit (in the absence of stress) to obtain an expression for the piezoresistivity. We find that the stress dependence can be represented in terms of the fractional change in Fermi energy:

$$\frac{\Delta\rho}{\rho_0 |\vec{\mathbf{X}}|} \approx -\frac{2\Delta E_F}{E_F |\vec{\mathbf{X}}|} \approx -2 \sum_{i,j} \frac{A_i S_{ij}}{E_F}, \qquad (1)$$

where  $\rho$  is resistivity,  $\vec{\mathbf{X}}$  is stress, and  $E_F$  is the Fermi energy. The right-hand side of Eq. (1) results from using a deformation-potential model when the band edges have overlapped. The second approximately equal sign is used because  $\Delta E_F$ would be exactly equal to the change in overlap (or  $-\Delta E_G$ , where  $E_G$  is the now negative energy separation between bands) only if the density of states of the conduction band were infinite, whereas it is merely much larger than that of the valence band.<sup>11</sup> For use in Eq. (1) we calculated the Fermi energy from the carrier (hole) concentration using the Fermi-Dirac integrals<sup>24</sup> because, as can be seen from Table I, the Fermi energies are not enough larger than thermal energy to justify use of the simple algebraic relation between carrier concentration and energy which holds in the degenerate limit. We obtained the hole concentration from experimental resistivity and Hall data using the relation

$$n_h = [\rho(300 \text{ K})/\rho] (\frac{1}{300} T)^{3/2} [0.9/eR_H(300 \text{ K})], (2)$$

where  $R_H(300 \text{ K})$  is the Hall coefficient at 300 K.<sup>11</sup> The  $(\frac{1}{300}T)^{3/2}$  factor and the 0.9 factor were chosen to be in accord with the analysis of Ref. 11. (Table I gives values of quantities we used in calculating piezoresistivities.)

Equating piezoresistivities measured parallel to the *c* axis and *a* axis at 475 K to the appropriate forms of Eq. (1) we obtain the following values for the deformation potentials:  $A_1 = 2.9 \text{ eV}$  and  $A_3$ = -1.8 eV. It is difficult to estimate the uncertainty in these values, but it might be quite large, especially in the case of  $A_3$  (perhaps ±30%). This

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T (K)	$R_H$ (cm <sup>3</sup> /C)	ρ(300 K)/ρ <sup>a</sup>	$n_h$ (10 <sup>20</sup> cm <sup>-3</sup> )	<i>E<sub>F</sub></i> (eV)	<i>S</i> <sub>11</sub> <sup>b</sup>	$(10^{-13})^{\rm b}$	$S_{13}^{b}$ m <sup>2</sup> /dyn)	S <sub>33</sub> <sup>b</sup>
300	0.080	1	0.70					
460		5.7	7.6	0.033	6.7	1.5	-6.3	13.7
475		9.5	13	0.070	6.9	1.7	-6.5	13.9
500		14.5	22	0.11	5.8	0.50	-4.5	10.0

TABLE I. Values of quantities in Eq. (1) and (2).

<sup>a</sup> Average of values in the c direction and a direction.

<sup>b</sup> Calculated from elastic data in Ref. 5.

is because the  $A_i$ 's are quite sensitive to how electrical data are used to deduce the carrier concentration and thereby the Fermi energy. The above values for the deformation potentials are similar to those found for semiconducting Ti<sub>2</sub>O<sub>3</sub> at 77 K ( $A_1$ =2.2 eV and  $A_3$ =-1.5 eV) and in agreement with those obtained from a reanalysis<sup>25</sup> of elastic constant data<sup>5</sup> through the transition.

To test the validity of the Fermi-level motion interpretation we used Eqs. (1) and (2) to calculate the piezoresistivities at 500 K for compression in the  $\tilde{c}$  and  $\tilde{a}$  directions and at 475 and 500 K for compression in the  $\tilde{d}$  direction. The results are shown in Fig. 1. From Fig. 1 it can be seen that the calculated points agree well with our data. (In fact even a value calculated at 460 K for the  $\tilde{d}$ direction agrees well with experiment as can also be seen in Fig. 1. This is probably fortuitous in view of the rather small Fermi energy (see Table I) and the fact that values calculated for the  $\tilde{c}$  and  $\tilde{a}$  directions at 460 K are about 50% larger in magnitude than the experimental ones.)

The piezoresistivities which we measure with hydrostatic pressure (shown in Fig. 3) are also consistent with there being strain-induced carrier redistribution between bands. In fact our hydrostatic data give qualitative evidence for the absence (or at least unimportance) of complications in the band structure. This is because such complications would cause observable effects only in the case of uniaxial stress.

Before ending Sec. IV we would like to point out that we have tried to determine if various other effects might be causing, or at least making a significant contribution to, the piezoresistivity. Among these effects are deviation from intrinsic behavior—as occurs in p-type InSb,<sup>26,27</sup> for example—interband scattering,<sup>28</sup> hole-electron scattering,<sup>29</sup> screening by charge carriers,<sup>30</sup> and the presence and disappearance of conduction-band polarons<sup>13</sup> or excitons.<sup>19,31</sup> Analysis indicates that the piezoresistivities due to these effects will not explain our results because they have the wrong sign, are too small, and/or do not have a suitable temperature dependence.

## V. CONCLUSION

Piezoresistivity of large magnitude and unusual temperature dependence occurs in  $Ti_2O_3$  as the semiconductor-semimetal transition is approached and traversed. It can be explained in terms of Fermi-level motion associated with strain-induced redistribution of charge carriers between valence and conduction bands. Fits of simple expressions to the piezoresistivity measured with uniaxial compression above 460 K yield very reasonable deformation potentials.

We conclude that the amount of band overlap is actually much smaller than that used in some previous analyses of other properties of  $Ti_2O_3$  at the SC-SM transition. This conclusion is based not only on the results presented herein but also on<sup>25</sup> the successful interpretation of thermalexpansivity data and reanalysis of elastic-constant data which will be described in more detail in future publications.

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