$$\sum_\nu \epsilon_2^{(\nu)} = \sum_\nu \epsilon_4^{(\nu)} = \sum_\nu \epsilon_6^{(\nu)} = 0 \ , \qquad \text{(A8)}$$

and

$$\sum_\nu \epsilon_3^{(\nu)} = \tfrac{4}{3}\sqrt{3}\,\epsilon_1^\gamma \ , \qquad \text{(A9)} \qquad\qquad \sum_\nu \epsilon_5^{(\nu)} = 8(\tfrac{2}{3})^{1/2}\epsilon_1^\gamma \ . \qquad \text{(A10)}$$

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†Supported in part at American University under NASA Grant No. NGR-09-003-014.

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Raman Study of the Semiconductor-Metal Transition in Ti₂O₃[†]

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(Received 6 July 1970)

The Raman spectrum of Ti₂O₃ exhibits seven modes as predicted for the corundum structure. The persistence of all seven of these modes above the semiconductor-metal transition temperature indicates no space-group change on going through the phase transition. The A_{1g} mode at 269 cm⁻¹ (300 °K) exhibits a significant frequency change (about 16%) and a large intensity increase relative to the other modes in the temperature range of the semiconductor-metal transition. These results are interpreted in terms of electronic and structural changes during the phase transition.

INTRODUCTION

Several physical properties of Ti₂O₃ undergo a rapid change over a range of 150 K° in the neighborhood of 400 °K. These include the lattice parameters,[1] the specific heat,[2] and the resistivity.[3] Below this range of temperature the material is a semiconductor and above this range the temperature dependence of the resistivity indicates metallic behavior.

We report here a study of the Raman-active modes, in frequency as well as in intensity, across the transition range. The study provides further information as to the nature of the change and agrees well with a previous model.

EXPERIMENTAL RESULTS

Surface Raman scattering was done using various (4579–5145-Å) excitation lines of an argon-ion laser. Single-crystal, oriented, and polished samples were used with the incident and scattered light propagat-
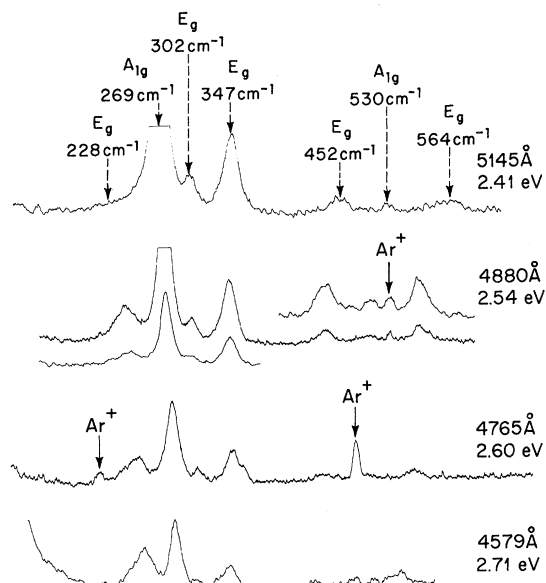
FIG. 1. Raman spectra of Ti_2O_3 at 300 °K. Momentum transfer is along c axis.

ing along the c axis. No differences in the spectra were observed for propagation along the a and b axes. Low temperatures were achieved with the sample in a cold stream of helium gas while high-temperature spectra were recorded with the sample in a high-temperature oven containing nitrogen gas. For the strongest laser lines, a slightly defocused beam helped minimize local sample heating.

Figure 1 shows the Raman spectrum of Ti_2O_3 at 300 °K using various excitation lines of an argon laser. Seven modes were observed whose polarization properties were consistent with the D_{3d} point-group symmetry of the corundum structure: five E_g modes at 228, 302, 347, 452, and 564 cm^{-1}, and two A_{1g} modes at 269 and 530 cm^{-1} (the frequency given in wave-number units). A strong resonant enhancement of the 228-cm^{-1} E_g mode relative to the other modes is observed for laser energies up to 2.71 eV. This resonance appears to be associated with a peak in ϵ_2 at 2.9 eV as determined by Scouler and Raccah[4] from reflectivity measurements.

As the sample temperature was increased across the critical transition range, a number of important observations were made. First, all the Raman modes could be followed across the transition and were still present above it (see Fig. 2). Further-more, no new modes were observed within a factor of 10 in intensity of the weakest line. Two other observations are shown in Fig. 3, where the frequency and intensity (relative to the other Raman modes) of the first A_{1g} (269-cm^{-1}) mode are plotted as a function of temperature. No relative intensity change was observed among all the other Raman modes. While some "softening" of all the modes

was observed in the transition region, the 269-cm^{-1} A_{1g} mode had the largest relative change. The frequency shift with temperature below the transition temperature range is attributed to the usual an-harmonic frequency pulling effects.

DISCUSSION

Calorimetric data[2] have shown that there is no latent heat in the semiconductor-to-metallic transi-tion in Ti_2O_3, indicating that it is not a first-order transition. Recent work[5] has shown no indication of a magnetic transition. The Raman observations reported here imply that there is no change in *point-group symmetry*, while the existing x-ray evidence,[1] having no superstructure lines for the high-temperature phase, shows that the *translation-al periodicity* is conserved across the transition. In the Landau theory of displacive second-order phase transitions, the symmetry of the crystal at the transition point must either increase by adding sym-metry elements or decrease by subtracting elements such that the space group of the crystal on one side of the transition is either a subgroup or a supergroup of the space group on the other side. In addition, this change must take place through an infinitesimal modification of the crystal structure. The only space group with the D_{3d} point-group symmetry and the same translational periodicity which bears this sub- or supergroup relationship to the corundum space group D_{3d}^6 is D_{3d}^4, which is this case is a subgroup of D_{3d}^6. However, it can be shown that the Ti_2O_3 struc-
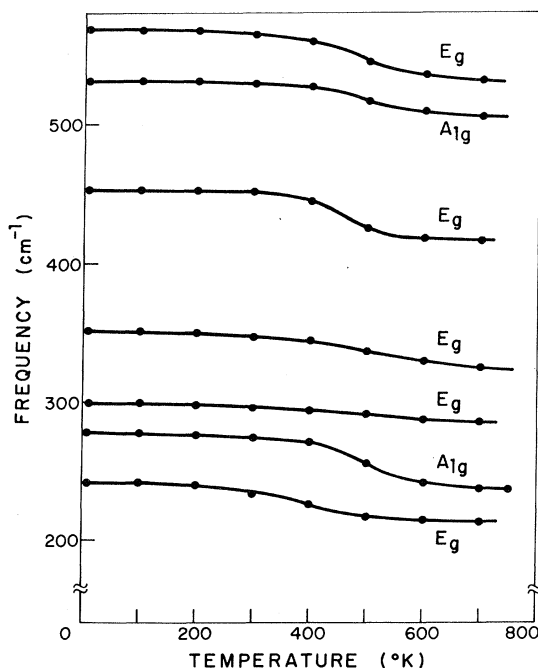

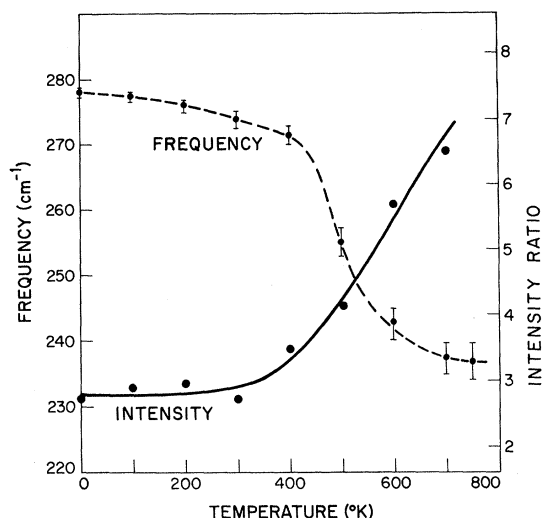FIG. 2. Temperature dependence of Raman-mode frequencies in Ti_2O_3.

FIG. 3. Frequency of A_{1g} mode and integrated intensity relative to the other Raman modes as a function of temperature.

ture cannot be modified by an infinitesimal deformation such that it has the symmetry D_{3d}^4. Such a symmetry change requires a macroscopic rearrangement of the atoms in the unit cell which is not allowed within the Landau theory[6] of displacive second-order transitions.

In addition to the possibility of a higher-order displacive transition, two other possibilities remain. The first is that the rapid change in physical properties observed is a phase transformation where the ordering parameter is electronic. In this case, Raman observation would not give information as to the order of the transformation, as in the case of a superconductive or magnetic transformation. The second possibility is that no derivative, of any order, of the free energy presents a discontinuity in that temperature range. In this case, there would be no transformation in the Ehrenfest sense.

This point of view is presented in another paper,[7] where a simple several-band Hubbard-type model, based on an earlier energy-level model proposed by Goodenough,[8] is used to yield a qualitatively good description of the previous experimental results[1,2] as well as the frequency behavior in our results of Fig. 2. We would like to show here that not only the Raman frequencies but also the intensities are consistent with Goodenough's model.

The structure consists of alternate layers of oxygen and titanium ions. The oxygen ions are hexagonally close packed and the titanium ions are in distorted octahedral interstices that share common faces along the hexagonal c axis. Two titanium atoms are succeeded along the c axis by a vacancy, while the distances between titanium ions in the

basal plane are equal to their distances in Ti metal. Previous considerations by Goodenough[7] on the c/a ratio in Ti_2O_3, V_2O_3, and Cr_2O_3 have already established that the lone $3d$ electron in Ti^{3+} forms a Ti-Ti homopolar bond along the hexagonal c axis.

Also shown in Fig. 4 is Goodenough's energy-level model for Ti_2O_3 in which the experimental values given for the various transitions have been obtained by Scouler and Raccah.[4] The outer s and p orbitals are split by a large energy gap between a filled $O^{2-}2p$ band and an empty titanium $4s$ band. The d orbitals are split by the cubic component of the crystalline fields into higher-energy e_g orbitals, which are directed toward nearest-neighbor anions, and lower energy t_{2g} orbitals, which are directed toward near-neighbor cations. The t_{2g} orbitals are split by the trigonal component of the field into a_{1g} orbitals directed along the c axis and e_g orbitals directed toward near neighbors in the basal plane. With four atoms per unit cell, the translational symmetry splits the a_{1g} band in two as shown. Symmetry allows splitting of the e_g band, but this is not shown because it should be small. Note that with one d electron per Ti^{3+} ion, the lower a_{1g} band is just filled. The relative positions of the a_{1g} and e_g bands vary with the crystallographic c/a ratio, and the semiconductor-to-semimetal transition occurs in Goodenough's model when the lower a_{1g} band enters the e_g band. At room temperature Ti_2O_3 is a semiconductor, and the a_{1g} band is below the e_g band (see Fig. 4).

The A_{1g} vibrational modes correspond to a beating against one another of the Ti atoms in pairs along the c axis. This motion has a c-axis component only. Simultaneously the oxygens forming triangles between each Ti pair are moving alternately away and towards one another. This motion has no c-axis component. Clearly a mode in which the oxygen atoms move out when the Ti atoms move in would have a lower frequency than one in which they would do the opposite. This is probably the main difference between the low-frequency $(l)A_{1g}$ mode and the high-frequency $(h)A_{1g}$ mode which are observed.

In the l mode, the screening effect of the oxygens is lowest, their motion greater for a given energy of vibration, and therefore the modulation of the trigonal component to the crystalline field, by the motion, is greatest. This would affect most the $3d$ electrons, which are the most polarizable, and in a phenomenological model, where the intensity of the Raman mode would be related to the polarizability of the electron cloud, this would be consistent with the stronger relative intensity of the l mode.

In Goodenough's[8] model, the $3d$ electrons are in the orbitals of a_{1g} symmetry along the c axis. As they are excited from the filled a_{1g} band into the empty e_g band (Fig. 4) with increasing temperature,
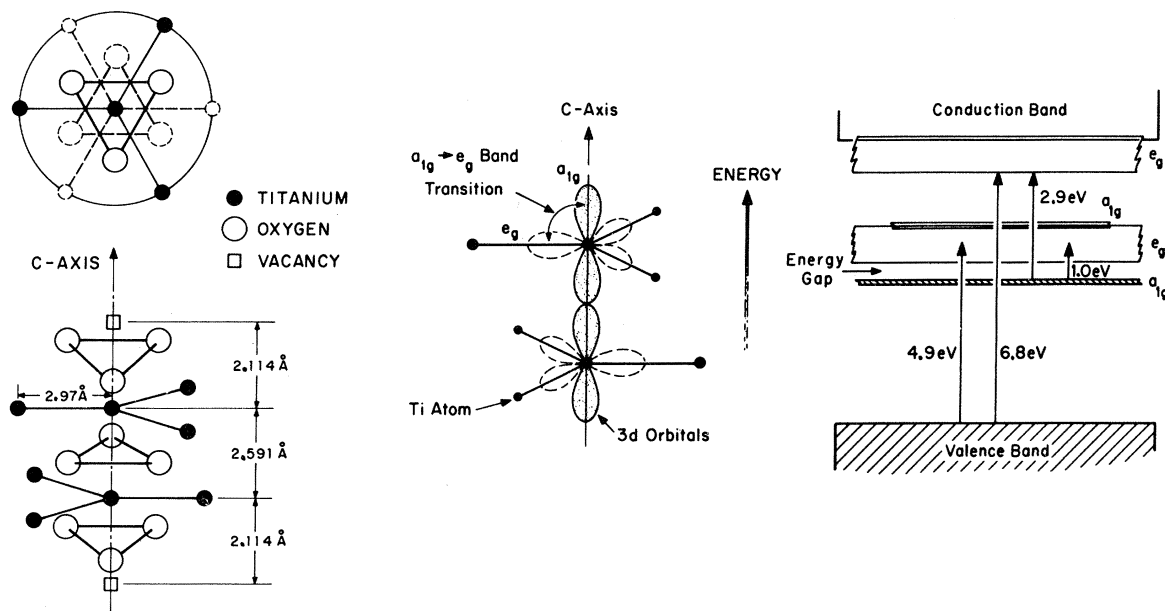
FIG. 4. Left: crystal structure of Ti_2O_3; center: electronic configuration of Ti_2O_3; right: electronic band structure of Ti_2O_3.

there is less screening between Ti ions along the c axis and a broadening of the potential well. Hence, a softening of the mode occurs together with an expansion of the c axis.

Finally, as electrons are redistributed by thermal excitation between the c axis and the basal plane as the lower a_{1g} band approaches and enters the e_g band, we observe an increase in the relative intensity of the first Raman A_{1g} mode. A preliminary interpretation of this fact could be that there is an increased polarizability created by the sharing of the $3d$ electron between the c axis and basal-plane orbitals. The strong resonance of only the 228-cm^{-1} E_g mode at room temperature would tend to eliminate a temperature-dependent electronic transition as a possible explanation for the A_{1g} mode intensity.

The Raman technique has allowed us to check the existing model in some of its qualitative aspects. Furthermore, the quantitative character of our results could be used to check a more formal theory now in progress.[7] An application to the V_2O_3 transition is in progress, and a similar Raman spectrum was observed at 300 °K with the most intense mode being an A_{1g} mode at 240 cm^{-1}.

†Work sponsored by the Department of the Air Force.
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