PHYSICAL REVIEW B VOLUME 10, NUMBER 12 15 DECEMBER 1974

Electrical properties and the metal-insulator transition in $(Sc_xTi_{1-x})_2O_3$[†]

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(Received 10 June 1974)

The resistivity, thermoelectric power, and lattice parameters of Ti_2O_3 doped with varying amounts of scandium have been measured between 77 and 700 K. A metal-to-insulator transition has been encountered in all specimens between approximately 400 and 600 K. The magnitude of the transition is nearly independent of Sc doping up to 0.33 at.% and grows with further increase in Sc content of the specimens. The activation energy for conduction at first declines and then increases with increasing Sc content. Since Sc doping has no large effect on the transition temperature, it is concluded that the transition is largely lattice dominated.

I. INTRODUCTION

A considerable body of information has become available concerning the gradual metal-semiconductor transition encountered in Ti_2O_3. This includes electrical resistivity studies,[1-5] thermoelectric measurements,[2,6] x-ray crystallography,[2,7-10] thermodynamic investigations,[11-13] infrared and Raman spectroscopy,[2,14-16] ultrasonic velocity and attenuation studies,[17,18] neutron diffraction,[19-22] and magnetic measurements.[2,23-31] While there was originally a diversity of interpretations concerning the nature of the transition, the model generally accepted at present involves the closing of a small band gap with increasing temperature due to a gradual distension of the lattice. At temperatures above the transition the two bands overlap sufficiently to give rise to metallic properties.

In this transition the question arises whether the change in properties is initiated by a redistribution of charge carriers among bands, which then produces a distortion of the lattice, or whether this causal sequence is reversed. One cannot ordinarily answer this type of question by experiments on doped material because the doping itself usually results in metallic behavior. Interestingly, however, the addition of V to Ti_2O_3 in small amounts has been found to alter the semiconductor-metal transition only gradually. Various types of experiments[6,13,32] carried out on the $V_xTi_{1-x}O_{1.5}$ system generally are in consonance with the interpretation[32-34] that the transition is dominated by the lattice. As x is increased the size of the semiconductor-metal transition is gradually reduced, as is the activation energy for the resistivity at low temperatures. However, the range of temperature over which these transitions occur is scarcely influenced by the addition of V_2O_3. Thus, crystals for which $x \lesssim 0.055$ still exhibit vestigial transitions precisely in the same temperature range as the parent compound. The replacement of Ti by V increases the c/a ratio of the lattice parameters and also the charge carrier density. This is manifested by a considerable decrease in resistivity of $V_xTi_{1-x}O_{1.5}$ relative to pure Ti_2O_3 at low temperature. If the transition were initiated by the conduction-electron population one might reasonably anticipate a progressive shift in the transition temperature range with the increasing carrier density concomitant to an increase in x, contrary to observation. For $x \gtrsim 0.06$ the material is metallic over the entire temperature range under study.

The experiments described below were carried out on Sc-doped Ti_2O_3. As in the case of V doping, the transition temperature is observed to be relatively unaffected by scandium addition. Unlike the V-doped Ti_2O_3 case, however, the Sc-doped material at low temperature remains an intrinsic semiconductor over the whole range of possible doping [(0–4) at.%]. The resistivity behavior indicates that large changes in excited-electron populations occur just below the onset of the transition, without any significant concurrent shift in transition temperature. Hence these data again suggest that the transition mechanism is indifferent to the electronic structure.

II. EXPERIMENTAL PROCEDURE

Undoped and Sc-doped Ti_2O_3 single crystals were grown in a commercial resistance-heated furnace under gettered argon using the Czochralski-Kyropoulos technique. The method as applied to the present problem is described by Reed *et al.*[35] and in greater detail by Lonney.[36] The starting materials were TiO_2 (99.999% pure, Johnson Mathey Chemicals Ltd., London), Ti (99.995% pure, Atomergic Chemetals Co., New York) and Sc_2O_3 (99.9% pure, Ventron Corporation). The total impurity content of the resulting boules was generally in the range of 100–300 parts per million atomic (ppma), as determined by commercial mass-spectrometric analyses. The Sc-Ti ratio was ascertained by scanning electron microscopy. The stoichiometry, as determined by oxidizing a known weight of the sample in pure O_2 at 1000 °C to constant weight, was in the range of $TiO_{1.505\pm0.003}$. In these determinations, advantage was taken of the fact that Sc_2O_3 cannot be oxidized to a higher valence state; hence the mass increase on weighing and the known Sc/Ti ratio sufficed to determine the sample stoichiometries completely.

Standard four-probe electrical resistivity measurements as a function of temperature were carried out by the method described by Chandrashekhar *et al.*[32]; the thermoelectric power was measured by a bridge technique also described elsewhere.[6] The lattice parameters were calculated from powder diffraction patterns obtained with a Norelco x-ray diffractometer, employing Cu$K\alpha$ radiation.

The resistivities of the several samples as a function of temperature are shown in Fig. 1. Several features are immediately apparent: (a) At temperatures below 350 K the material remains a semiconductor for all levels of doping. This behavior contrasts sharply with that which obtains upon doping with vanadium,[32] as already discussed in the Introduction. (b) The metal-insulator transition and the metallic conductivity are relatively insensitive to scandium content; from 0 up to 0.04 Sc fraction, the transition point, as measured by the steepest slope, changes less than 25°. The metallic resistivity above the transition increases by about 10% in this indicated doping range. (c) The conductivity in the insulating state and its temperature behavior are significantly affected by scandium. The lowest temperature resistivity is changed by an order of magnitude; as shown in Table I, the activation energy ϵ varies by about a factor of 5. Furthermore, the variation of ϵ with doping level is nonmonotonic. As scandium is introduced, ϵ at first drops rapidly until a concentration of $x = 0.003$ is reached and then gradually recovers. (d) Below 200 K, all ϵ become independent of temperature. Between 200 and 300 K, however, the activation energies if anything tend to decrease slightly with increasing temperature.

The thermoelectric effects are exhibited in Fig. 2. Above 250 K the Seebeck coefficients α for all specimens are closely coincident. The sharp dropoff to small values above 400 K is correlated with the semiconductor-metal transition in the material. The sizable increase in α for curves 1 and 2 of Fig. 2 at low temperature is quite comparable to that described in Ref. 6, where this property was attributed to phonon drag effects. In the present case these are manifest for $x = 0$ and 0.0001 but not for higher values.

The above electrical properties may be roughly correlated with crystallographic observations. These are summarized in Fig. 3, where c, a, and the ratio of c-to-a parameter for the unit cell at room temperature are plotted against x. It is seen that the c/a ratio decreases monotonically from a value of 2.640 at $x = 0$ to a constant value of 2.635 at $x \gtrsim 0.004$.[37] In the range where this ratio de-

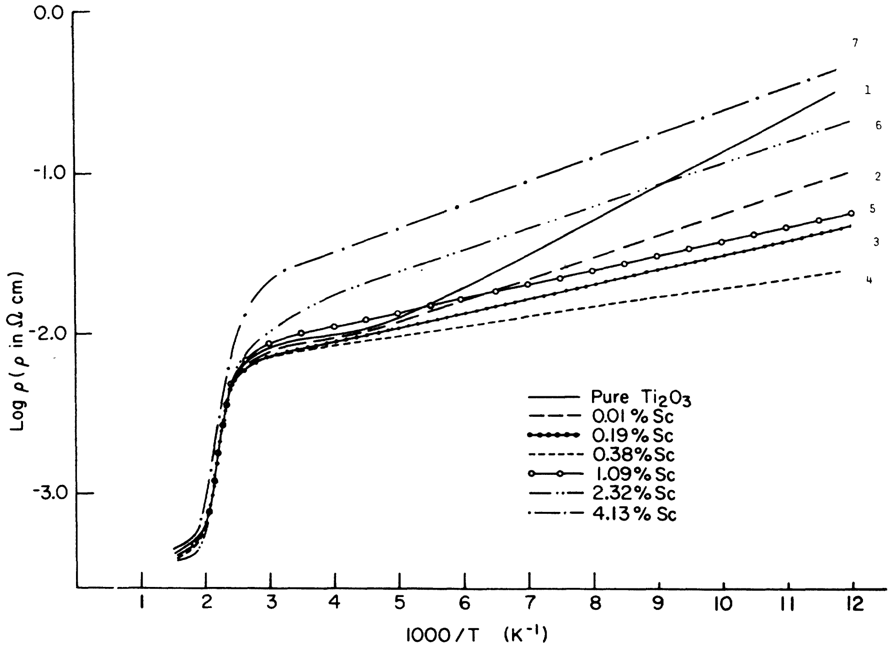

FIG. 1. Plots of $\log_{10}\rho$ vs $1/T$ for $(Sc_xTi_{1-x})_2O_3$ in the range $0 \leq x \leq 0.0413$. Curve 1: pure Ti_2O_3. Curves 2–6: 0.01-, 0.19-, 0.38-, 1.09-, 2.32-, 4.13-at.% Sc in Ti_2O_3.

TABLE I. Activation energies of Sc-doped Ti_2O_3 samples. Stoichiometry analysis: Samples heated to TiO_2 in O_2 at 925 °C. All samples have composition $(Sc_x Ti_{1-x})O_{1.505 \pm 0.003}$.

	x in $Sc_x(Ti_{1-x})O_{1.5}$		
	In melt[a] (at.%)	In solid[b] (at.%)	Activation energy (eV)
1	0	···	0.0490
2	0.03	0.01	0.0265
3	0.1	0.19	0.0188
4	0.33	0.38	0.0113
5	1.0	1.09	0.0180
6	2.5	2.32	0.0265
7	4.0	4.13	0.0278

[a] By chemical addition.

[b] By scanning electron microscopy of Sc/Ti ratio. Error is ±0.02.

creases the activation energy for the resistivity below room temperature also diminishes, as shown in curves 1-4 in Fig. 1.

III. DISCUSSION

Except for the region very close to the metal-insulator transition the slopes of $\log_{10} \rho$ vs $1/T$ all are constant or *decrease* with increasing temperature. In a change from extrinsic to intrinsic conduction, one would anticipate an increase in slope over a temperature range in which the number of intrinsic carriers becomes comparable to the number of scandium ions. As will be argued below, the experiments cover this range for several samples; however, no such increase in slope is experimentally detected.

Considerable information on the conduction and valence bands of pure Ti_2O_3 is available from various sources. As discussed below in greater detail, these bands are e- and a_1-like, respectively, separated by a gap of the order of 100 meV[6,13,17] which seems to depend somewhat on sample preparation. The a_1 valence band has an effective hole mass near the band edge of $(3-4)m_0$[4,17]; the conduction-band-electron mass is higher by about a factor of 3.[13,17] These facts enable us to determine whether or not, for a given temperature, conduction should become intrinsic: When the number of thermally excited electrons becomes larger than the dopant concentration, the intrinsic conduction regime has clearly been reached. On the other hand, if donor or acceptor states are present with activation energies less than half the gap, the number of intrinsic carriers at lower temperatures must eventually fall below the number of excited impurity states and the conduction must become extrinsic. When this happens, the slopes of the $\log_{10} \rho$-vs-$1/T$ curves must diminish.

For parabolic bands the number of intrinsic carriers is given by

$$n_i^2 = 4 \left(\frac{(2\pi)^2 m_c m_v (kT)^2}{h^4} \right)^{3/2} e^{-\epsilon_g/kT} .$$

At the low-temperature range of our data, this formula yields a carrier density of $n \approx 10^{16}$ cm^{-3}.

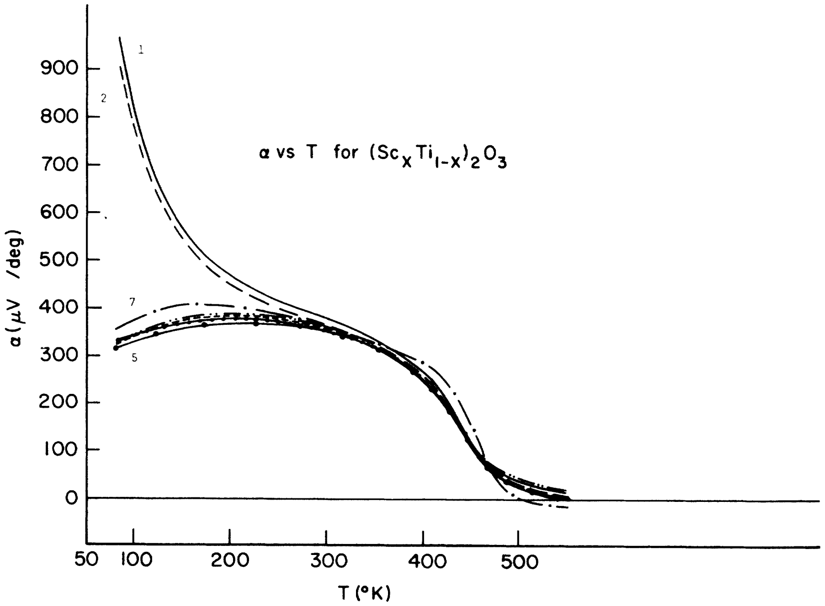

FIG. 2. Plots of Seebeck coefficients α vs $1/T$ for $(Sc_x Ti_{1-x})_2O_3$ in the range $0 \le x \le 0.0413$. See Fig. 1 for key to different curves.

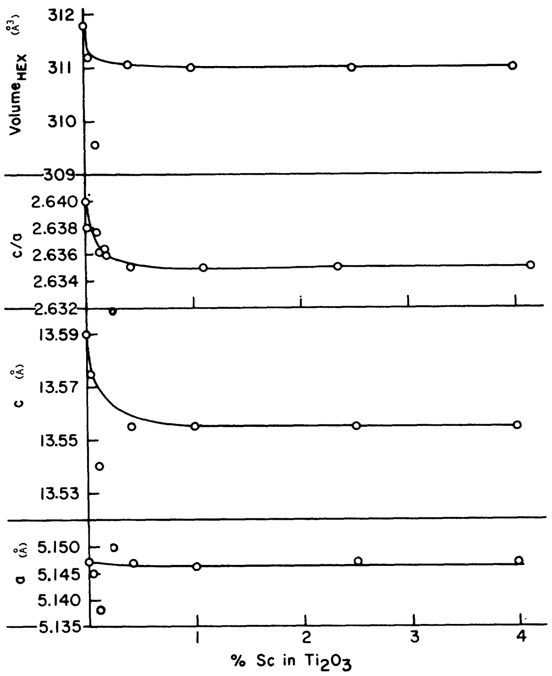

FIG. 3. Volume, c/a, c, and a parameters as a function of Sc doping (at.%) in Ti_2O_3 at room temperature (Ref. 37).

At 300 K, just before the transition, we obtain $n \approx 10^{19}$–10^{20} cm^{-3}, depending on the ϵ_g value. Comparing these numbers to the scandium concentrations of 4.0×10^{18} to 1.6×10^{21} cm^{-3}, one should reasonably expect substantial changes of slope in the resistivity curves, so long as each scandium ion introduces of order unity impurity states.

Since these anticipated changes of slope are not encountered in the temperature range below the transition, one is forced to conclude either that scandium ion introduces no impurity levels in the gap, or that, if present, the activation energies for thermal promotion of carriers into the bands exceed $\frac{1}{2}\epsilon_g$. In either case, the material should then be intrinsic over the whole range of temperatures and concentrations investigated. We may then conclude that the slopes of the log ρ-vs-$1/T$ curves are proportional to $\frac{1}{2}\epsilon_g$ for all samples.

We cannot obtain the carrier densities from the resistivity curves of Fig. 1, because the mobility must obviously vary among the samples. There is a general trend toward higher resistivity with increased scandium concentration which we attribute to the increased number of impurity-scattering centers. Moreover, we do not know quantitatively the extent to which phonon scattering reduces mobility. The shoulder on the pure Ti_2O_3 resistivity (curve 1) has elsewhere been ascribed[6] to temperature-dependent phonon scattering. This effect is masked in the other samples by the large impurity scattering. At and slightly above room temperatures the increasing number of carriers from the decreasing gaps and the decreasing mobility due to the greater scattering in samples with intermediate Sc doping cancel each other. The dependence of the carrier density on the gap is fractionally more pronounced at lower temperatures, and there the approximate cancellation effect no longer occurs.

As the temperature of all specimens is increased beyond 400 K the resulting band overlap dominates all of the above-mentioned effects. The charge-carrier density is now so high that shielding largely eliminates the ionized impurity-scattering phenomena, so that all curves nearly coincide.

From the above it follows that incorporation of substantial quantities of Sc into Ti_2O_3 only slightly affects the electric properties of the host in the semiconducting regime and scarely influences the temperature range of the electrical transition. These observations reinforce the earlier contention,[32] based on studies of the V_2O_3-Ti_2O_3 system, that the transition is largely dominated by the lattice.

The thermoelectric effects displayed in Fig. 2 may also be interpreted on the same basis. The large peak in the Seebeck coefficient for the pure material has previously[6] been ascribed to phonon drag effects; this peak can no longer be maintained for $x > 0.0001$. The Fermi level of all specimens remains within or very close to the narrow gap for the semiconducting regime and is pinned by the band overlap in the semimetallic regime. For this reason, the various curves closely coincide in Fig. 2 (excepting specimens exhibiting the phonon drag effect below 200 K).

It has been shown earlier[6] that the thermoelectric results of the type displayed in Fig. 2 are not inconsistent with a near-intrinsic pure-band semiconductor model for $T < 400$ K, and with an intrinsic band-overlap model for $T > 500$ K. Thus it emerges that the various features described in the earlier publications may again be used successfully to interpret the experimental findings in Sc-doped Ti_2O_3.

Figure 4 shows the behavior of the activation energy as a function of scandium concentration. The behavior is complex. Between 0 and 0.5 at.% the activation energy variation follows the crystallographic changes in c/a ratio. This variation, like the crystallographic distensions, saturates above 0.5 at.% Sc, and a slower variation with the opposite sign emerges. It is thus clear that at least two distinct processes are involved in the dependence of the activation energy on doping. We have inter-

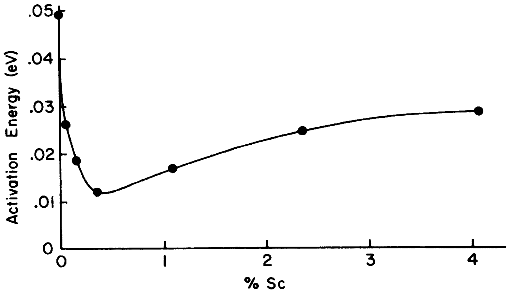

FIG. 4. Activation energy vs scandium doping (at.%) in Ti_2O_3.

preted the activation energy as a band gap; hence the band gap seems to depend on doping in a nonmonotonic fashion.

The Fermi energy of Ti_2O_3 lies among the d levels of the Ti^{3+} ion. These d levels are split first roughly into two higher (e_g) and three lower (t_{2g}) levels by the approximately cubic crystal field of the oxygen ions around each metal ion in the corundum structure. The oxide is strongly ionic, so the three t_{2g} levels certainly lie below the two e_g levels; the Fermi energy lies among the lower three levels. However, the actual crystal field involves an additional component of trigonal symmetry. The three lower levels are thus further split by the trigonal field into an a_1 level below and two e levels above. This order must be assigned because the pure material is an insulator.[38] The Fermi energy actually lies between these split levels; hence, the band gap contains first a contribution originating from the trigonal field splitting, V_3. Next, account must be taken of the fact that along the c axis of the corundum lattice sets of Ti atoms are paired off to form Ti_2O_3 units. Within each Ti_2O_3 molecular unit, the d states on the two metal ions strongly overlap. This interaction splits what would otherwise be two degenerate states into bonding the antibonding molecular orbitals. This splitting is relatively large and is different, in general, for the a_1 and e states. Hence, the energy gap occurs between the a_1 *bonding* and e *bonding* states. This contribution to the gap is given by $\frac{1}{2}(V_a - V_e)$, where V_a and V_e are the respective molecular interactions. Finally, the molecular states somewhat more weakly overlap states on other nearby molecules. It is this interaction which broadens the molecular levels into bands. The band gap is thus reduced as the split levels "spread" into bands. The resultant band gap is therefore

$$\epsilon_g = V_3 + \tfrac{1}{2}(V_a - V_e) - \tfrac{1}{2}W_a - \tfrac{1}{2}W_e ,$$

in which W_a and W_e are the respective bandwidths. There are thus three qualitatively different interactions involved in establishing a band gap. Further investigation would be required to determine precisely which interactions are involved in the separate aspects of the dependence of band gap on Sc doping. The fact that ϵ_g changes after c and a have attained constant values for $x \gtrsim 0.0033$ simply indicates that the activation energy depends on factors other than those measured by lattice parameters.

ACKNOWLEDGMENTS

The authors are very grateful to G. Yuochunas for providing the single crystals needed in this study and to Professor P. H. Keesom for many stimulating discussions. They wish to thank Dr. A. P. B. Sinha for assistance in the x-ray measurements.

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†Supported by the National Science Foundation under Grant No. GH34731.

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