PHYSICAL REVIEW VOLUME 187, NUMBER 3 15 NOVEMBER 1969

Electrical Properties of Some Titanium Oxides*

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(Received 17 March 1969; revised manuscript received 14 July 1969)

Electrical conductivity, differential thermal analysis, ac Hall effect, and x-ray diffraction measurements were used to investigate the low-temperature behavior of flux-grown single crystals of the titanium oxides. Monoclinic Ti_3O_5 and the triclinic Magnéli phases Ti_4O_7, Ti_5O_9, and Ti_6O_{11} were studied—with the major effort devoted to Ti_4O_7. The only known property of the Magnéli phases was the magnetic susceptibility, which was measured on polycrystalline samples. Several transitions, most of which correlate with previously reported magnetic susceptibility data, were found in these compounds. A semiconductor-to-metal transition occurs in Ti_4O_7 at 149°K, followed by a second transition at 125°K which involves some structural rearrangement. The properties of these compounds are discussed in relation to existing theories for the transition-metal oxides. It is concluded that the observed properties are not adequately explained by these theories.

I. INTRODUCTION

MANY transition-metal oxides have been found to be insulators in cases where band theory would predict a partially filled 3d band and metallic conductivity. When these oxides are made semiconducting either by deviations from stoichiometry or by addition of metal ions of different valence, they exhibit the characteristic of very low mobility. The theories developed to explain the behavior of these materials have been reviewed in a recent article by Adler and Brooks.[1] Another characteristic of some transition-metal oxides is the semiconductor-to-metal transition such as that found in Ti_2O_3 and in the vanadium oxides by Morin.[2]

The existence of the "Magnéli phases" in the titanium-oxygen and vanadium-oxygen systems was reported in 1957 by Andersson *et al.*[3] These are a homologous series of triclinic phases of compositions Ti_nO_{2n-1}, with $4 \leq n \leq 10$. They are bounded by monoclinic Ti_3O_5 on the one side and by reduced rutile (TiO_{2-x}) on the other. The Magnéli phases are built up of TiO_6 octahedra which share corners and edges to form slabs of rutile that can be extended infinitely in two directions. In the third direction, these slabs have a finite width of n TiO_6 octahedra, where n is the integer in the chemical formula. These slabs are bordered by a layer of octahedra which share faces with the octahedra in the last layer of the slab and comprise the first layer of the next slab. This causes the titanium-atom positions in one slab to correspond to unoccupied or interstitial positions in the next slab, and decreases the symmetry from tetragonal to triclinic while increasing the size of the unit cell.

Previous magnetic susceptibility measurements on sintered bodies[4] and powders[5] of these phases indicated the presence of low-temperature transitions in several of them. In addition, Ti_3O_5 was known to undergo a phase transition at 460°K which involved some structural change.[6] The present paper reports some electrical measurements on single crystals of several of these compounds in the temperature range where phase transitions occur.

II. EXPERIMENTAL METHODS

Single crystals of Ti_3O_5, Ti_4O_7, Ti_5O_9, and Ti_6O_{11} were obtained by flux-growth methods.[7] The largest crystals were of the order of 0.2×0.5×5 mm, with the longest dimension being along the *b* axis. Ti_3O_5 has a maroon-black color while the Magnéli phases are a very deep blue. Four-terminal dc conductivity measurements were made along the *b* axis for each phase and in one direction perpendicular to the *b* axis for Ti_4O_7. Measurements were taken from 78 to 295°K and, in the case of Ti_3O_5, to 480°K. The contacts consisted of 40-gauge copper wires soldered to the crystal with indium, except for the high-temperature measurements for which a conductive Epoxy was used. Because many crystals contained voids or pipes, the conductivity values are accurate only to some tens of percents.

Differential thermal analysis was also used to observe the low-temperature phase transitions. A brass sample holder containing wells for the sample and a standard (TiO_2 powder) had a cold-finger extension on the bottom. Cooling was accomplished by submerging the cold finger in liquid N_2. For the heating cycle, the holder was removed from the liquid N_2 and allowed to warm up to room temperature.

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* Work conducted at the Materials Research Laboratory, Pennsylvania State University, and supported by the U. S. Atomic Energy Commission. Based on a thesis submitted by one of the authors (R. F. B.) in partial fulfillment of the requirements for the Ph.D. degree in physics.

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TABLE I. Low-temperature x-ray-diffraction data for Ti_4O_7. *hkl* = Miller indices; *d* = observed *d* spacings; I/I_0 = relative intensities (%).

hkl	295°K *d* (Å)	295°K I/I_0	250°K *d* (Å)	250°K I/I_0	165°K *d* (Å)	165°K I/I_0	140°K *d* (Å)	140°K I/I_0	102°K *d* (Å)	102°K I/I_0	86°K *d* (Å)	86°K I/I_0
$10\bar{2}$	4.274	63	4.283	71	4.268	80	4.287	39	4.283	37	4.281	41
$\bar{1}03$	···	···	···	···	···	···	···	···	3.428	95	3.427	76
$1\bar{2}0$	3.378	66	3.384	98	3.375	98	3.384	75	3.384	22	3.382	32
103	···	···	···	···	···	···	···	···	3.045	34	3.047	41
$12\bar{2}$	3.020	32	3.024	34	3.021	32	3.023	66	3.022	27	3.022	20
$10\bar{4}$	2.817	49	2.817	71	2.814	66	2.823	100	2.822	59	2.819	51
022	···	···	···	···	2.794	54	2.798	32	2.797	46	2.798	41
200	2.627	22	2.630	34	2.625	39	2.624	32	2.623	85	2.622	98
104	2.521	100	2.527	27	2.520	29	2.518	37	2.520	12	···	···
120	2.473	49	2.477	20	2.471	32	2.466	34	2.468	15	2.468	17
$02\bar{4}$	2.422	24	···	···	···	···	2.421	20	2.424	17	2.424	17

Low-temperature x-ray diffraction and ac Hall-effect measurements were performed on Ti_4O_7. The diffraction was done on powdered Ti_4O_7 to which germanium powder was added as an internal standard. The Dewar, designed for x-ray measurements to liquid-helium temperature, was equipped with beryllium windows and mounted on a General Electric XRD-5 diffraction unit. A calibrated platinum resistance thermometer was used to determine the sample temperature.

The Hall effect was measured using an ac sample current at either 100 or 500 Hz. A bucking circuit, which provided a voltage adjustable in amplitude and phase, was used to correct for misalignment of the Hall probes. A Princeton Applied Research model HR-8 lock-in amplifier was used with a Princeton Applied Research AM-1 impedance matching transformer as the detector. To detect the Hall voltage of about 50 nV, it was necessary to fasten all leads very rigidly so as to minimize induced voltage due to motion of the wires in the magnetic field.

III. EXPERIMENTAL RESULTS

A. Ti_4O_7

The results of conductivity measurements parallel to the *b* axis on two single crystals of Ti_4O_7 are shown in Fig. 1. Several other crystal measurements substantiated these results. Conductivity perpendicular to the *b* axis was about one-third as great. Ti_4O_7 is metallic at room temperature and at (149±2)°K undergoes a phase transition to a semiconducting state with a corresponding three-orders-of-magnitude decrease in conductivity.

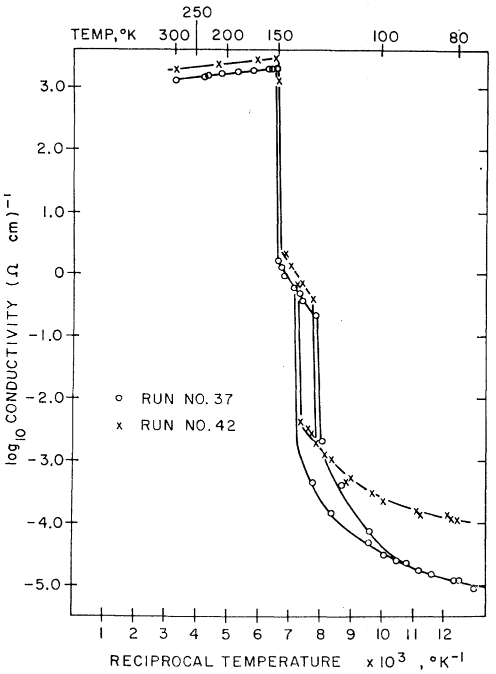

FIG. 1. Conductivity parallel to the *b* axis of two single crystals of Ti_4O_7 selected from two growth runs (cf. Ref. 7).

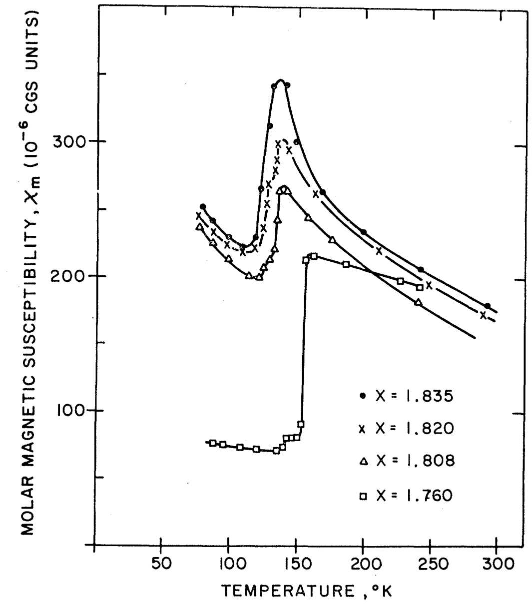

FIG. 2. Magnetic susceptibility of some titanium oxide powders (after Vasil'ev and Ariya, Ref. 4).

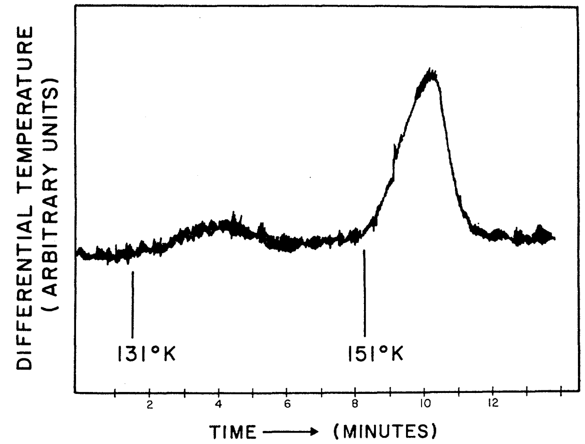

FIG. 3. Tracing of differential-thermal-analysis curve for Ti_4O_7.

At this transition there is also a sharp drop in the magnetic susceptibility of Ti_4O_7. The susceptibility data of Vasil'ev and Ariya[4] for compounds that are close to Ti_4O_7, Ti_5O_9, and Ti_6O_{11} in composition are reproduced in Fig. 2 for comparison wlth the conductivity data. Recently, Danley[8] measured the magnetic susceptibility of Ti_4O_7 crystals from the same crystal-growth runs as those used for the electrical measurements reported here. He obtained results similar to those of Vasil'ev and Ariya for $TiO_{1.760}$, except that his value for the transition temperature agreed closely with the present conductivity and differential thermal analysis results.

At about 125°K there is another transition which causes a decrease in the conductivity by three orders of magnitude, but with no observable change in susceptibility. This second transition exhibits a thermal hysteresis of 8 to 10°K.

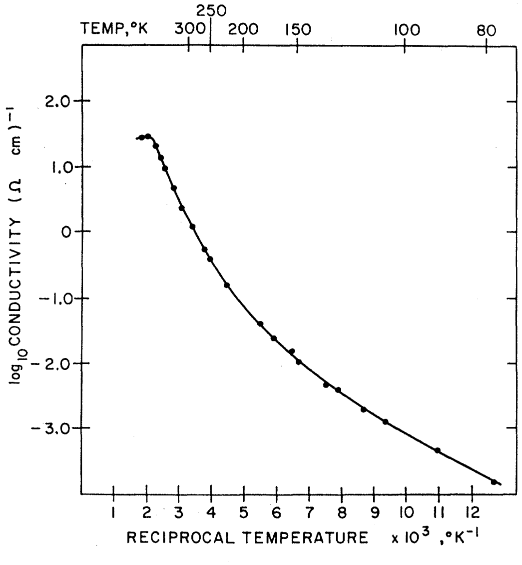

FIG. 4. Conductivity of a single crystal of Ti_3O_5.

The results of the x-ray diffraction measurements are presented in Table I. There is no observable structure change at the first (high-temperature) transition. Below the second transition two new peaks become visible which correspond closely to the calculated *d* spacings for the 103 and $\bar{1}03$ reflections. This indicates that some structural rearrangement has occurred, changing the structure factor for these reflections. Both transitions were observed on the heating cycle by differential thermal analysis as shown in Fig. 3, but the low broad peak corresponding to the low-temperature transition was not visible on the cooling cycle.

Hall-effect measurements gave a room-temperature mobility of 1 cm^2/V sec, increasing to 4 cm^2/V sec at 160°K. These values are in reasonable agreement with the value of 0.55 cm^2/V sec calculated from conductivity data on the assumption of one free electron per Ti^{3+} ion. Below the first transition no Hall voltage could be detected and an upper limit of 10^{-2} cm^2/V sec was placed on the mobility.

B. Ti_3O_5

The conductivity of single crystal Ti_3O_5 was measured from 78 to 480°K. These results are shown in Fig. 4. Ti_3O_5 undergoes a semiconductor-to-metal transition at about 460°K. The slope of the conductivity curve increases sharply as the transition is approached from the low-temperature side but there is no abrupt increase in the value of the conductivity at the transition. The reported magnetic susceptibility of Ti_3O_5 increases sharply at this temperature and is independent of temperature above and below the transition.

C. Ti_5O_9

The conductivity of Ti_5O_9 from 78 to 295°K is shown in Fig. 5. It can be seen that two distinct transitions,

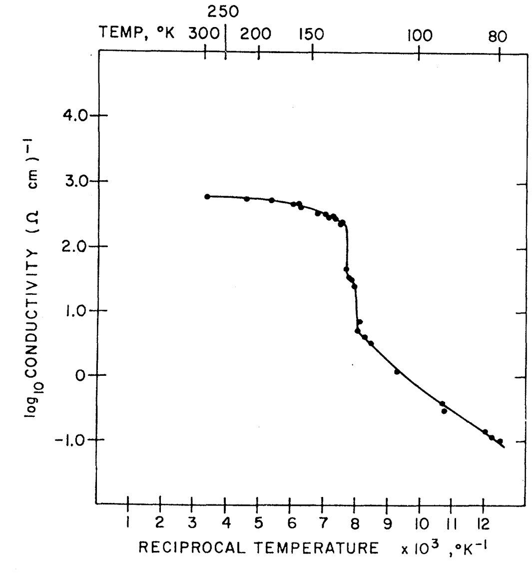

FIG. 5. Conductivity of a single crystal of Ti_5O_9.

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[8] W. J. Danley (private communication).

separated by about 5°K, occur in Ti_5O_9. These separate transitions are also visible on the tracing of the differential thermal analysis results shown in Fig. 6 and in the magnetic susceptibility data of Vasil'ev and Ariya ($TiO_{1.808}$ and $TiO_{1.820}$ in Fig. 2).

D. Ti_6O_{11}

The conductivity of Ti_6O_{11} from 78 to 295°K is shown in Fig. 7. The transition temperature is about 130°K, as determined by conductivity measurements, but magnetic-susceptibility measurements and differential thermal analysis give a lower value.

E. Ti_8O_{15}

Ti_8O_{15} was obtained by reduction of rutile single crystals at 1300°C in a mixture of carbon monoxide and carbon dioxide. x-ray measurements revealed the presence of low-angle grain boundaries in this material. Thus the Ti_8O_{15} can be considered as polycrystalline with a preferred orientation. This material was found to be semiconducting over the temperature range 78–295°K as shown in Fig. 8. The activation energy is 0.087 eV.

IV. DISCUSSION

In this section experimental results are compared with existing theories. The latter, as mentioned earlier, have been reviewed in considerable detail by Adler and Brooks[1] and will therefore be only very briefly summarized here.

A variety of theories have explained the low-conductivity phases in terms of "localization" of the electronic states. Such theories attribute low conductivity to low mobility and thus account nicely for the observed low mobilities of carriers added by doping. They do not account in a natural way for the abrupt transition to metallic conduction found in some of the oxides but can, as stated by Adler and Brooks, be extended to include this feature. The extensions, however, tend to be *ad hoc* and qualitative.

A second class of theories follow the more conventional band model ("itinerant-electron model") and attribute the insulating state to the absence of partially filled bands. One subsequent major problem is that of explaining how the *d* band can be split into subbands such that the lowest one has just enough states to accommodate the electrons available. In a general way, this can be done by crystal-field splitting provided the symmetry is low enough. Two symmetry-lowering mechanisms that have received consideration are antiferromagnetic ordering[9] and structural distortion. It should be noted that this class of theories does not account for the low mobility of extrinsic carriers. The great advantage, however, is that the transition to a metallic state

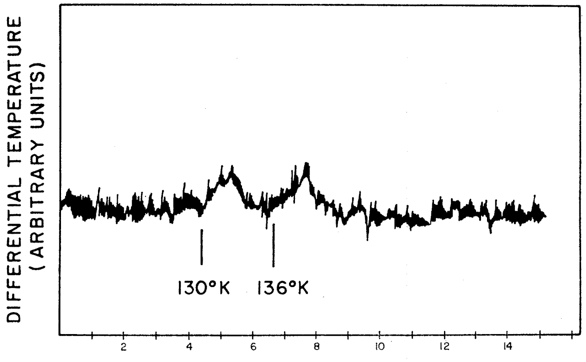

FIG. 6. Tracing of differential-thermal-analysis curve for Ti_5O_9.

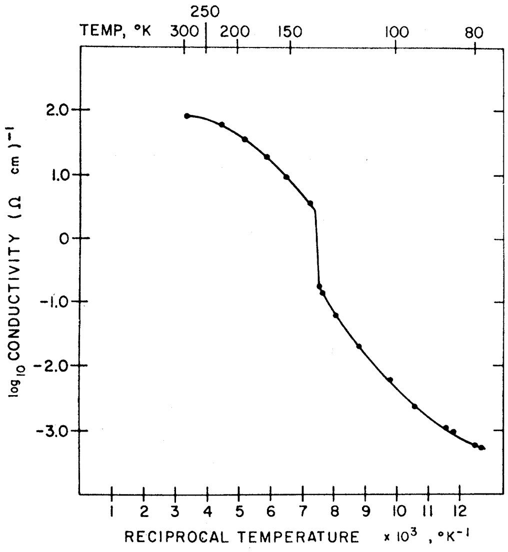

FIG. 7. Conductivity of a single crystal of Ti_6O_{11}.

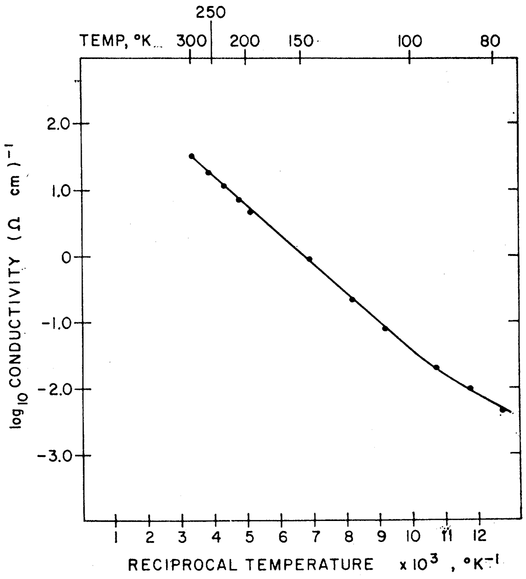

FIG. 8. Conductivity of polycrystalline Ti_8O_{15}.

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[9] J. C. Slater, Phys. Rev. **82**, 538 (1951).

follows in a natural way, as shown by Adler and Brooks. The crux of their argument is that whenever the energy gap is pressure-dependent, it must also depend on carrier concentration and will disappear when enough carriers are thermally excited across it.

In the following paragraphs, we consider the present results in terms of these ideas.

A. Ti_3O_5

Ti_3O_5 is not one of the Magnéli phases, but is a "neighboring" composition. x-ray diffraction and magnetic susceptibility measurements show that a phase transition occurs in Ti_3O_5 in the vicinity of 460°K. This transition involves some structural change and recent susceptibility measurements by Danley[8] indicated that it also exhibits thermal hysteresis. The present electrical data for conditions above room temperature were obtained using conducting Epoxy contacts. These deteriorated at 480°K, so that data were taken only on the heating cycle and the thermal hysteresis could not be observed.

Ti_3O_5 is metallic with a conductivity of 35 $(\Omega\ \mathrm{cm})^{-1}$ just above the transition. If it is assumed that each Ti^{3+} ion has contributed a *d* electron to the conduction band, a value of $2.3\times10^{22}/\mathrm{cm}^3$ is obtained for n and the calculated mobility is 9.6×10^{-3} cm^2/V sec. This is much less than the lower limit of about 1 cm^2/V sec set by the uncertainty principle for validity of the band model.[10] Otherwise, it appears that the electrical behavior can fit into the framework of the Adler-Brooks theory.

B. Ti_4O_7

In attempting to apply the Adler-Brooks theory to Ti_4O_7, the first of the Magnéli phases, one immediately runs into difficulties. In the first place, there is no observable structural change at the first transition. The magnetic susceptibility does change sharply but its behavior does not resemble that of an antiferromagnet. Rather, it closely resembles the susceptibility of V_2O_3 which, according to the most recent study,[11] is not antiferromagnetic. (For a different point of view, see the discussion on V_2O_3 by Adler.[12]) The second transition is definitely accompanied by some structural distortion, but this is a transition between two semiconducting states rather than a semiconductor-to-metal transition.

Another difficulty involves the questionable validity of the band model in the semiconducting state in view of the very low mobility. Thus the properties of Ti_4O_7 are not very satisfactorily explained by the Adler-Brooks model. It appears that a localized model may be a more accurate description of the semiconducting state in this as in many of the other transition-metal oxides.

Goodenough's theory[13] considers the amount of overlap between the *d*-electron wave functions of neighboring cations to be the critical parameter for determining whether the *d* electrons are collective or localized. He has developed an empirical formula for the critical interionic distance R_c that separates the collective from the localized state. For $R>R_c$ the electrons should be localized and for $R<R_c$ the electrons should form a band. R_c is given by the formula

$$R_c^{3d}=[3.20-0.05m-0.03(Z-Z_{\mathrm{Ti}})-0.04S(S+1)]\ \text{Å}.$$

Here m is the average valence of the cations, equal to 3.5 for Ti_4O_7, and S is the average spin of the cations, equal to $\frac{1}{4}$. The formula yields a critical Ti-to-Ti separation of 3.01 Å. There are several Ti-to-Ti distances less than this in Ti_4O_7; hence, the theory predicts that it should be metallic, in agreement with observation. Goodenough predicted that a semiconductor-to-metal transition might take place in the Magnéli phases at lower temperatures if the Ti^{3+} ions in the shear layers moved towards each other and trapped the *d* electrons in homopolar bonds between them. In this case, two *d* electrons would be shared by two adjacent Ti^{3+} ions. This is a possible explanation for the *second* transition in Ti_4O_7, in which some structural rearrangement was observed. If this is so, it appears that some other type of localization must become energetically favorable sooner to account for the observed semiconductor-to-metal transition at the higher temperature.

C. Ti_5O_9 and Ti_6O_{11}

Ti_5O_9 and Ti_6O_{11} differ from Ti_4O_7 only by the increased repeat distance between shear layers and the slight decrease in unbonded *d*-electron concentration. A marked difference is seen in the properties of phases which are very similar in structure and electron concentration. The conductivities of both Ti_5O_9 and Ti_6O_{11} increase with increasing temperature above the transition so that these do not appear to be true semiconductor-to-metal transitions. Ti_5O_9 undergoes two transitions separated by 5°K and the conductivity decreases by a factor of 50 over-all. Ti_6O_{11} undergoes a single transition resulting in the same amount of conductivity change. The magnetic susceptibilities of these two phases are very similar with the exception of the double transition in Ti_5O_9. Below the transition, the susceptibilities of Ti_5O_9 and Ti_6O_{11} start to increase again with decreasing temperature while the susceptibilities of Ti_3O_5 and Ti_4O_7 appear to be temperature-independent in the low-temperature phase. The fact that slight changes in structure or electron concentration can alter the properties so markedly suggests that there are competing interactions which must be very close in energy. This is borne out by the double transitions in Ti_4O_7 and Ti_5O_9.

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[10] R. H. Tredgold, *Space Charge Conduction in Solids* (Elsevier Publishing Co., Inc., New York, 1966).

[11] H. Kendrick, A. Arrott, and S. A. Werner, J. Appl. Phys. **39**, 585 (1968).

[12] David Adler, Rev. Mod. Phys. **40**, 714 (1968).

[13] J. B. Goodenough, Mater. Res. Bull. **2**, 37 (1967); **2**, 165 (1967); Czech. J. Phys. **B17**, 304 (1967).

D. Ti_8O_{15}

The conductivity of Ti_8O_{15} is activated over the whole temperature range investigated. The activation energy of 0.087 eV could be involved in exciting the d electrons into a band from a localized state, or it could be associated with an activated mobility with the electrons hopping from one localized state to another.

V. SUMMARY

Several transitions have been observed in single crystals of the titanium oxides by electrical conductivity measurements and differential thermal analysis. Most of these transitions correspond closely with the transitions observed in previously reported magnetic susceptibility data obtained on powders or sintered pellets of these compounds. The one notable exception is the lower-temperature transition in Ti_4O_7 which has been shown to involve some structural rearrangement without affecting the magnetic susceptibility.

The behavior of Ti_4O_7 is similar to that of V_2O_3 except that Ti_4O_7 undergoes two separate transitions. The first involves a change in magnetic susceptibility, while the second involves structural rearrangement with no change in susceptibility. It was pointed out that existing theories apparently do not provide a satisfactory explanation of the semiconductor-to-metal transition in Ti_4O_7 or account for the properties of Ti_5O_9 and Ti_6O_{11}. The striking changes brought about by relatively small structural alterations in this series of materials suggest that highly detailed theoretical treatments will be needed for any satisfactory degree of understanding.

ACKNOWLEDGMENTS

Thanks are due to Professor M. E. Bell and Professor H. K. Henisch for many helpful discussions, to Dr. Robert Newnham for advice on x-ray methods, and to Mr. William Danley for making his magnetic susceptibility data available to us. The support of the U. S. Atomic Energy Commission is also gratefully acknowledged.

PHYSICAL REVIEW VOLUME 187, NUMBER 3 15 NOVEMBER 1969

Quantum Corrections in the Theory of the Anomalous Skin Effect

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(Received 5 December 1968)

A comparison is made between the semiclassical and the quantum-mechanical treatment of the anomalous skin effect. The latter theory is based on the density matrix. The author calculates the value of the surface impedance with both theories. The difference depends on a parameter λ, which is the ratio of the skin depth to a typical de Broglie wavelength. This wavelength corresponds to the velocity component, normal to the surface, of an effective electron. The order of magnitude of the correction depends on the relaxation time, and can amount to 10% for sufficiently pure metals.

1. INTRODUCTION

BECAUSE much information about the structure of solids is obtained by means of electric conductivity measurements in the frequency region of the anomalous skin effect (ase), it is obvious that a proper description of these experiments is needed. In the literature two different approaches have been followed for treating the ase: (i) the semiclassical approach, which is based on the concept of the distribution function,[1] and (ii) the quantum-mechanical approach founded on the density matrix.[2,3] It has been reported by several authors[4] that no significant discrepancies exist between the treatments. In this paper it is shown that this conclusion is not correct. The reason for this is the fact that the motion of electrons, close to the boundaries, was not properly accounted for in Ref. 2. This is because use has been made of the "speculum assumption," defined in Sec. 2, which is not correct for a quantum treatment, as is shown in Secs. 6 and 7. Although the subject of the ase has tended to become almost "classical," it should be emphasized at this point that the treatments given in the textbooks are fundamentally incorrect for this reason. In order to make a quantitative comparison between the two approaches, let us confine our attention to the value of the surface impedance of an electron system with a metallic density. In order to make it clear at which point the present analysis differs with the existing ones, a formal description is given of the response of the electron system to an applied electromagnetic field. In Sec. 3 the relation between this response and the surface impedance is established. In Secs. 4 and 5 a brief

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