JOURNAL OF SOLID STATE CHEMISTRY 12, 265–269 (1975)

Magnetic Susceptibility and EPR Spectra of Titanium Oxides: Correlation of Magnetic Parameters with Transport Properties and Composition*

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Received July 11, 1974

Magnetic susceptibility and electron paramagnetic resonance (EPR) parameters have been correlated with electrical conductivity and X-ray structural data to elucidate some of the transport properties of a number of the Magnéli phases of the titanium–oxygen system. The concentrations of localized and delocalized electrons at both high and low temperatures are reported, as are estimates of the effective electronic mass. These results have been used to show that the low-temperature conductivity is consistent with a hopping model. For temperatures above the electronic transitions, the mobility and conductivity are reasonably described by assuming combined optical-mode-phonon and ionized-defect scattering effects. It is suggested that many of the characteristics of the oxides such as the transition temperatures are related to the magnetic exchange energy J between $[Ti^{3+}V_oTi^{4+}]^{+1}$ centers and the $[Ti^{3+}–Ti^{3+}]$ clusters (with constrained antiferromagnetism) and the composition of the oxides.

Introduction

It is well known that several of the discrete phases in the Ti_nO_{2n-1} series (where $n = 3$–$n = 10$) exhibit semiconductor to metal transitions (*1–4*). Mulay and co-workers (*4–7*) have extensively studied the static magnetic susceptibility of these phases, and Bartholomew and Frankl (*3*) have reported on the single-crystal electrical conductivity of a number of them. Rao et al. (*8*) have studied the electrical conductivity of pressed pellets of Ti_3O_5. In addition, a detailed X-ray study of the structure of Ti_4O_7 has been reported recently (*9, 10*).

Houlihan and Mulay (*11–14*) and others (*8, 15–18*) have obtained additional electronic structural information on the Magnéli phases ($n = 4$–$n = 10$) of the Ti–O system by the application of electron paramagnetic resonance (EPR) spectroscopy. Houlihan and Mulay (*13, 14*) have shown that the observed EPR spectrum in these oxides is consistent with an electron localized near an oxygen vacancy, i.e., a $(Ti^{3+}–V_o–Ti^{4+})^{+1}$ center, with possible charge transfer between the two Ti sites.

In this paper we show that the magnetic parameters obtained from static magnetic-susceptibility and EPR measurements can be correlated with electrical conductivity and X-ray structural data so as to elucidate some of the transport properties of the Magnéli phases of the titanium–oxygen system.

Localized and Delocalized Electron Concentrations

Magnetic-susceptibility (*4–7*) and EPR (*13, 14, 17*) data indicate considerable spin-pairing of Ti^{3+} ions in the low temperature phases of the oxides, as first predicted by

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* This work is based on the doctoral theses in Solid State Science submitted by J. F. Houlihan (1973) and W. J. Danley (1972) to The Pennsylvania State University.

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Goodenough (*19*, *20*). Assuming a "spin-only" model, Mulay and Danley (*6*, *7*) have determined the number of localized and delocalized electrons for some of the high-temperature phases from magnetic susceptibility parameters. Comprehensive results on all of the phases studied so far are reproduced in Table I (*21*).

In the low-temperature phases, EPR and electrical-conductivity data (*3*) have been combined to obtain the number of "delocalized" or conduction electrons, n_0. Values of n_0 at $T \sim 120$ K are also listed in Table I. In addition, the EPR spin-concentration data allow for the calculation of the number of spin-paired electrons and those localized at $(Ti^{3+}-V_o-Ti^{4+})^{+1}$ centers (*22*).

Effective Electronic Mass

Applying the Pauli–Peierls relation for the temperature-independent paramagnetism (TIP) of the oxides in the high-temperature phases, Mulay and Danley (*6*, *7*) have estimated the effective electronic masses (Table I). Houlihan (*22*) has shown that this approach can be extended to the low-temperature phases and that the results are consistent with those obtained by assuming a degenerate electron gas and estimating m^* from n_0 and the energy gap, E_g, obtained from the data of Bartholomew and Frankl (*3*). Estimates of the effective masses in the low-temperature phases are also shown in Table I. It might be noted that these values are in reasonable agreement with the value of ~5 m_e obtained for the low-temperature phase of Ti_2O_3 by Yahia and Frederikse, who considered Hall effect and thermoelectric-power data (*23*).

Conduction Properties of the Ti–O Phases at Low Temperatures

It has been shown elsewhere (*14*, *22*) that a hopping mechanism is consistent with the conduction properties in the low-temperature phases. An estimate of the electron mobility for the hopping process has been obtained from (*20*)

$$\mu_{\text{hop}} = \frac{e a^2 \nu \exp(-E_A/kT)}{kT}, \qquad (1)$$

where a is the hopping distance (assumed to be approximately the Ti–Ti distance), ν is the hopping frequency and E_A is the activation energy for the process. Values of ν, and μ_{hop} are shown in Table II.

Combining the number of conduction electrons given in Table I and the μ_{hop} values of Table II, values of the anticipated electrical conductivity, σ, at ~120 K have been calculated and compared with the experimental data of Bartholomew and Frankl (*3*). These results are shown in Table III.

As can be seen, reasonably good agreement

TABLE I

PARAMETERS DERIVED FROM (A) MAGNETIC-SUSCEPTIBILITY (B) EPR DATA

	High temperature region (from A)			Low Temperature region (from B)	
Phase	Localized electrons (cm^{-3})	Delocalized electrons (cm^{-3})	m^*/m	(n_0) conduction electrons (cm^{-3})[a]	m^*/m
Ti_3O_5	0.00	2.29×10^{22}	22.4	9.1×10^{20}	6.7
Ti_4O_7	1.71×10^{21}	1.54×10^{22}	15.4	2.4×10^{21}	5.6
Ti_5O_9	1.10×10^{21}	1.24×10^{22}	19.5	1.7×10^{21}	6.4
Ti_6O_{11}	3.7×10^{21}	7.4×10^{21}	15.4	3.8×10^{21}	5.4
Ti_8O_{15}	3.85×10^{21}	4.6×10^{21}	13.2	5.3×10^{21}	12.5

[a] At $T = 120\ K < T_t$, except no T_t observed for Ti_8O_{15}.

TABLE II

Phase	Hopping frequency (ν) (Hz)	Hopping mobility (μ) (cm^2/V sec)
Ti_3O_5	4.9×10^{11}	7.0×10^{-5}
Ti_4O_7	1.6×10^{12}	4.0×10^{-6}
Ti_5O_9	9.3×10^{12}	4.2×10^{-4}
Ti_6O_{11}	1.4×01^{13}	2.7×10^{-7}
Ti_8O_{15}	1.5×10^{12}	2.1×10^{-4}

is obtained for Ti_3O_5, Ti_4O_5, and Ti_8O_{15}. However, for Ti_5O_9 and Ti_6O_{11} considerable discrepancy exists. In both cases the hopping model employed predicts a lower conductivity than is experimentally observed. This discrepancy is thought to be due to an increased impurity-band contribution to the mobility that results from larger localized-spin concentrations in Ti_5O_9 and Ti_6O_{11}, i.e., more $(Ti^{3+}\text{–}V_o\text{–}Ti^{4+})^{+1}$ centers, and thus increased overlap of defect-center wave functions (*24*).

Conduction Properties of Ti–O Phases at High Temperatures

At temperatures above the transition, mobility and conductivity values have been calculated on the basis of combined optical-mode-phonon and ionized-defect scattering effects (*14*, *22*) and these results are shown in Table III.

In the case of Ti_4O_7 the results are in excellent agreement with the experimental data. As will be discussed elsewhere (*25*), experimental difficulties reported by Bartholomew and Frankl (*3*) on measurements of Ti_3O_5 raise some question about the accuracy of their measurements on this oxide in this temperature range. Rao et al. have reported a value of $\sigma_{\text{measur.}} \sim 1.5 \times 10^1$ (ohm cm)$^{-1}$ for Ti_3O_5. However, since these measurements were made on pressed pellets, it is difficult to make any definite correlations.

For Ti_5O_9 and Ti_6O_{11} the results of Bartholomew and Frankl indicate that the transitions involved are "semiconductor-to-semiconductor" type transitions, i.e., an activation energy is required both above and below the transition. Hence, we are currently investigating the possibility of including a term incorporating what appears to be a hopping contribution to the total mobility. This procedure is consistent with our assignment of a hopping mechanism in Ti_8O_{15} at 120 K, since this compound exhibits no transition temperature.

An Overview of Structural Aspects, Electronic Properties, and the Exchange Interactions

Goodenough (*1*, *20*) predicted the possibility of finding, in the Magnéli phases, low-temperature spin pairing in homopolar Ti^{3+}–Ti^{3+} bonds. This concept is supported both

TABLE III

COMPARISON OF CALCULATED AND MEASURED CONDUCTIVITY PARAMETERS

	Low-temperature phase ($T = 120$ K)		High-temperature phase			
Oxide	σ calcd (ohm cm)$^{-1}$	σ^d measur. (ohm cm)$^{-1}$	μ calcd (cm^2/V sec)	μ^* measur. (cm^2/V sec)	σ^b calcd (ohm cm)$^{-1}$	σ^b measur. (ohm cm)$^{-1}$
Ti_3O_5	9.35×10^{-3}	5.5×10^{-3}	0.21^a	—	7.4×10^2	3.5×10^1
Ti_4O_7	1.49×10^{-3}	3.10×10^{-3}	0.6^b 4.1^c	1.0^b 4.0^c	1.48×10^3	1.5×10^3
Ti_5O_9	1.20×10^{-1}	6.3	0.76^b	—	1.54×10^3	5.5×10^2
Ti_6O_{11}	1.6×10^{-4}	7.0×10^{-2}	0.9^b	—	1.1×10^3	1.1×10^2
Ti_8O_{15}	1.77×10^{-1}	2.5×10^{-1}	—	—	—	—

[a] At $T = 450$ K.

[b] At $T = 300$ K.

[c] At $T = 160$ K.

[d] After Bartholomew and Frankl (*3*).

by the discovery (*6*, *7*) of a discontinuous drop $\Delta\chi$ in the magnetic susceptibilities and by the direct observation by Marezio et al. (*9*, *10*) of Ti–Ti pairing in Ti_4O_7. However, the pairing does not occur across the shear planes, as originally anticipated by Goodenough, but within the rutile slabs between shear planes. As n increases in the homologous series Ti_nO_{2n-1}, the discontinuity $\Delta\chi$ decreases, disappearing for $n \geqslant 7$. It is reasonable to assume that electrons tied up in homopolar bonds are not mobile, which is why in Table I the concentration of conduction electrons at low temperature can increase with decreasing Ti^{3+} concentrations. From EPR measurements (*22*) the localized unpaired-electron concentration is also seen to increase with decreasing Ti^{3+}-ions concentration.

As the concentration of Ti^{3+} ions decreases, so also does the energy to be gained from a cooperative formation of Ti–Ti pairs. Therefore, T_t decreases with increasing n in the series Ti_nO_{2n-1}, vanishing for $n \geqslant 7$.

The overall narrowing of EPR line widths for various phases with increasing concentration of Ti^{3+} was previously attributed to exchange-narrowing effects (*11*). The most likely mechanism for such narrowing would be between the $[Ti^{3+}-V_o-Ti^{4+}]^{+1}$ center and a $[Ti^{3+}-Ti^{3+}]$ cluster. It should be noted that the $[Ti^{3+}-V_o-Ti^{4+}]^{+1}$ center involves only one unpaired spin and, as postulated before (*6*, *7*), the $[Ti^{3+}-Ti^{3+}]$ cluster shows the possibility of "constrained antiferromagnetism" with nonzero localized spin density. We have estimated the exchange interaction parameter J from the single crystal EPR data (*22*) and the approximations of the exchange-narrowing methods, discussed recently by Samokhalov and Babushkin (*26*) and by Anderson and Weiss (*27*). Further details of this topic will be presented in a separate publication.

In Fig. 1 estimates of the exchange energy (J), the localized spin concentration (n) at $T \sim 120$ K and the transition temperature T_t are shown as a function of composition. As can be seen, J increases rapidly with Ti^{3+} concentration but not with n. Therefore, it appears that the nonzero spin density in $[Ti^{3+}-Ti^{3+}]$ clusters must also contribute to the measured J acting at the unpaired spin in the $[Ti^{3+}-V_o-Ti^{4+}]^{+1}$ center. This observation can be rationalized as mentioned before by introducing the concept of the "constrained" antiferromagnetism" for the $Ti^{3+}-Ti^{3+}$ pairs in the said clusters. Strong coupling within a pair may give rise to homopolar bonds with a net moment of zero. However, interactions with an unpaired, localized spin at a neighboring $[Ti^{3+}-V_o-Ti^{4+}]^{+1}$ center can induce some localization of the spin density within a $[Ti^{3+}-Ti^{3+}]$ cluster to produce an antiferromagnetic couple of weak atomic moment. As the number of interactions between the $[Ti^{3+}-V_o-Ti^{4+}]^{+1}$ centers and any homopolarly bonded $[Ti^{3+}-Ti^{3+}]$ clusters increases, the magnitude of the localized moment in such clusters is also expected to increase. These moments couple back onto the unpaired spin of the $[Ti^{3+}-V_o-Ti^{4+}]^{+1}$ centers to give an enhanced exchange narrowing, or larger J. Hence, J is seen to increase with the increasing concentration of Ti^{3+} ions as obtained from composition.

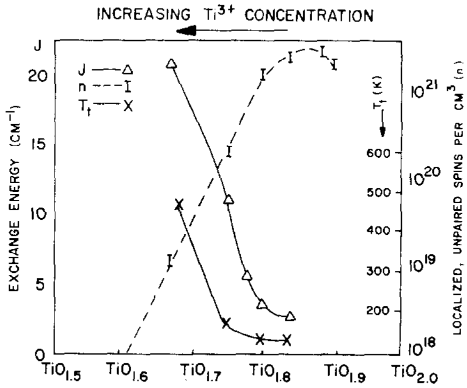

FIG. 1. Localized unpaired spin concentration (n), estimates of the exchange interaction (J), and the transition temperature (T_t) as a function of composition for titanium oxides.

The temperature, T_t, above which thermal agitation overcomes the exchange energy and breaks up the $[Ti^{3+}-Ti^{3+}]$ clusters would be expected to increase with the exchange energy, J. This is seen to be so in Fig. 1. Below an oxygen-to-titanium ratio of $\sim$1.83 (Ti_6O_{11}) the exchange energy is seen to increase rapidly in a manner similar to the transition temperature. This situation is reminiscent of the correlation between the exchange energy J and the Néel temperature, T_N, in classical antiferromagnetism. It is also interesting to note that only those oxides with an oxygen-to-titanium ratio equal to or below that of 1.83 (Ti_6O_{11}) exhibit semiconductor-to-metal transitions.

Thus as the temperature is raised, it appears that cooperative atomic displacements occur (*1*, *9*, *10*) and the homopolar bonds or partially spin-paired clusters are broken, releasing a considerable number of electrons into the conduction band. This results in significant increases in the electrical conductivity (*3*) and the static magnetic susceptibility (*4*–*7*) above the transition temperature.

Acknowledgments

Grants from the Central Fund and the Scholarly Activity Fund of the Pennsylvania State University to one of us (J. F. H.) have been useful in the final stages of this work. Early phases of this work were supported by the Atomic Energy Commission, U.S.A [Contract AT (3D-1)-2581 to L.N. Mulay].

We thank Dr. J. B. Goodenough for stimulating discussions and helpful advice in writing this paper.

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