

OXIDES WHICH SHOW A METAL-TO-INSULATOR TRANSITION AT THE NEEL TEMPERATURE

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In a previous paper¹ it was pointed out that the lower oxides of titanium and vanadium behave like metals. It was suggested that this was so because in the oxides at the beginning of the $3d$ series the nonbonding (t_{2g}) orbitals extend out far enough to overlap and form a narrow conduction band. It was also pointed out that polycrystalline samples of Ti_2O_3 and V_2O_3 appear to show a transition from metal to insulator at the Néel temperature. Now, this transition has been confirmed with single crystals of these oxides and also found to occur in the oxides VO and VO_2 . This Letter reports electrical conductivity measurements made on polycrystalline TiO,² and on single crystals of Ti_2O_3 ,³ VO, V_2O_3 , and VO_2 ,⁴ as additional evidence for the existence of a conduction band of t_{2g} orbitals, and suggests a model to explain the conductivity transitions which are found.

The single-crystal samples were 0.1 mm in size, too small for the usual four-point measurement, so two pressure contacts were used. Therefore, the absolute value of conductivity quoted is somewhat in doubt due to contact resistance and dimensional uncertainty. To obtain a Ti_2O_3 sample of suitable uniformity, a small fragment was broken from a large boule. It was unoriented. The vanadium oxide crystals were easily oriented from their growth habit. The TiO sample was a small rectangular bar and was measured by the four-point method.

Typical conductivity curves are shown in Fig. 1. In addition to these results, TiO was found to be a metal over the whole temperature range investigated: 300°K to 1.5°K. The transition temperatures from conductivity measurements are summarized in Table I and compared with those from heat capacity (C_p) and magnetic susceptibility (χ). In V_2O_3 and VO the transitions were very abrupt, with no measurable time or temperature dependence. In VO_2 and Ti_2O_3 the transitions were spread out over a range of temperature as shown in Table I, and some time dependence of conductivity was observed on cooling. Above the transition temperature, in the metallic state, all of the oxides showed a positive temperature coefficient of resistance typical of metals. If it is assumed that all the d electrons are available for

transport in this state, the electron mobility lies approximately in the range 10^{-1} (TiO) to 10^{-2} (VO) $cm^2/volt\ sec$ indicative of a very narrow conduction band. Finding a hysteresis about the Néel transition seems a little unusual. It should be recalled, however, that C_p and χ measurements have been made most frequently only with increasing temperature. The C_p entries and the first two χ entries in Table I are of this kind and compare well with the transition temperature

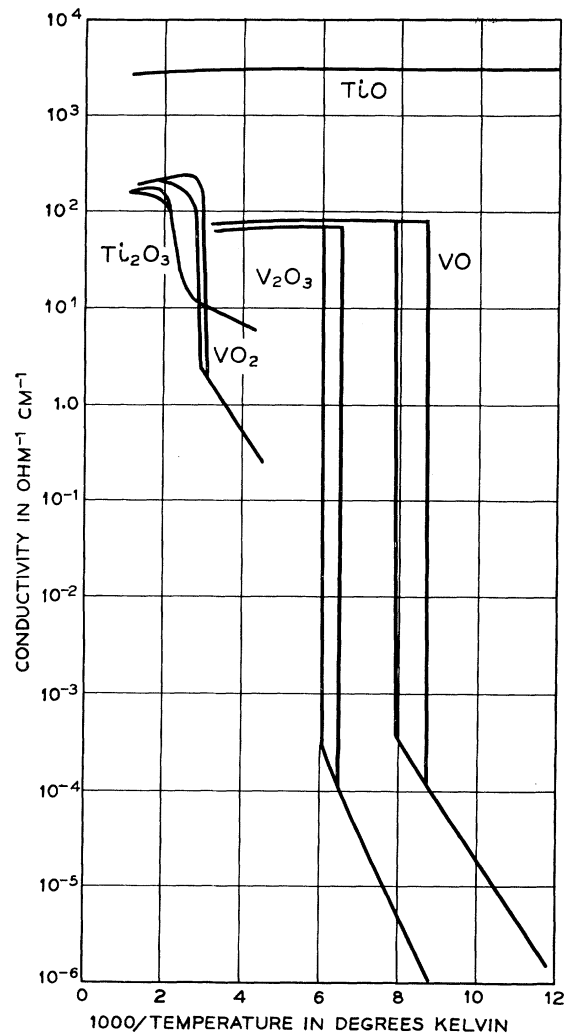


FIG. 1. Conductivity as a function of reciprocal temperature for the lower oxides of titanium and vanadium. Measurements were made along the [100] direction in VO, and along the c axis in V_2O_3 and VO_2 .

Table I. Conductivity transition temperatures in degrees Kelvin are compared with Neel temperature from heat capacity, C_p , and magnetic susceptibility, χ .

Oxide	Structure	Conductivity		C_p	χ
		cooling	heating		
TiO	rock salt
VO	rock salt	114	126
V ₂ O ₃	corundum	153	165	169 ^a	168 ^b
VO ₂	monoclinic ^c	340-325	335-350	340 ^d	340 ^e
Ti ₂ O ₃	corundum	500-400	400-500	473 ^f	390-490 ^g

^aC. T. Anderson, J. Am. Chem. Soc. **58**, 564 (1936).

^bJ. Wucher, J. recherches centre natl. recherche sci. Labs. Bellevue (Paris) **4**, 254 (1952).

^cSlightly distorted rutile structure; G. Andersson, Acta Chem. Scand. **10**, 623 (1956).

^dJ. Jaffray and A. Dumas, J. recherches centre

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^eE. Hoschek and W. Klemm, Z. anorg. u. allgem. Chem. **242**, 63 (1939).

^fB. F. Naylor, J. Am. Chem. Soc. **68**, 1077 (1948).

^gSee reference 2.

measured by conductivity on heating. The last χ entry was measured both with heating and cooling and shows a hysteresis.⁵

In TiO and VO, which are rock salt structures, each cation is connected to its twelve nearest neighbor cations by overlapping t_{2g} orbitals. In the metallic state these orbitals constitute a partially filled band. This band contains six states per atom and is one third full in TiO and one half full in VO. Let the crystal become an antiferromagnet with the spin alignment reversing between (111) planes of cations as found in NiO for example. Then electrons on one half of the nearest neighbors have spin up and on the other half have spin down. Thus the band is split into two sets of bands, one set for spin up and one set for spin down. In VO each set of bands contains three lower states per atom which are full and three higher states per atom which are empty. Thus VO is an insulator below the transition temperature. In TiO the lower bands are only two thirds filled so TiO shows no transition to an insulator. This model is similar to one suggested by Slater⁶ for MnO, in which each set of bands contains five lower states per atom which are filled and five higher states per atom which are empty. However, in MnO the t_{2g} orbitals do not overlap, the band width is zero, and the crystal is an insulator both above and below the transition.

The situation in the remaining oxides is much more complicated for reasons of structure and also because the transition in conductivity occurs

even though the t_{2g} orbitals are partially empty. A more general point of view has been suggested by Anderson⁷ and is based on the observation that antiferromagnets which involve indirect exchange are insulators. It is suggested that there are two processes in competition: (1) the correlation effect which tends to localize the d electrons and which is aided by setting the cation spins in an antiferromagnetic alignment; (2) the tendency of electrons to delocalize themselves by spreading into a band and thereby gaining kinetic energy. That these two processes are fairly energetic is indicated by the conductivity change of a factor 10^6 in VO and V₂O₃ at the transition. A splitting of the conduction band by ~ 0.4 eV is required to produce this amount of change in the carrier concentration. This may be compared with the energy of the Néel temperature which is only ~ 0.01 eV and which may represent the energy difference between the two competing processes. This more general point of view also offers an alternative explanation for the difference between TiO and VO. The electron mobility in TiO is ten times that in VO. This suggests that the conduction band is much wider in TiO so the electrons gain enough kinetic energy on spreading into it that the metallic state is always lower in energy than the antiferromagnetic state. The transition in all of the oxides can be described by a partially filled band which splits into an upper band which is empty and a set of lower occupied levels which are localized and have an antiferromagnetic spin alignment.

¹F. J. Morin, Bell System Tech. J. **37**, 1047 (1958).

²Sample obtained from A. D. Pearson and described in J. Phys. Chem., Solids **5**, 316 (1958).

³Sample obtained from Linde Company.

⁴Crystals of the vanadium oxides were grown by H. Guggenheim by the hydrothermal process.

⁵Additional evidence was obtained that a hysteresis at the Néel transition is not unusual. With R. G. Shulman the nuclear magnetic resonance of Co⁵⁹ in CoO

was measured with slow warming and cooling about T_N . The transition was gradual, and on cooling appeared to occur several °K below the warming transition.

⁶J. C. Slater, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 19.

⁷P. W. Anderson, Phys. Rev. (to be published) and private communication.

MULTILEVEL PULSED-FIELD MASER FOR GENERATION OF HIGH FREQUENCIES*

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A proposed^{1,2} multilevel pulsed-field ruby maser has been successfully operated at 4.2°K as an oscillator at both 12.61 kMc/sec and 19.15 kMc/sec with a pumping frequency of 12.61 kMc/sec. The results demonstrate the feasibility of generating or amplifying very high frequencies on a pulsed basis by conversion of magnetic field energy, supplied to an inverted spin distribution, into coherent radiation. The principles of operation and characteristics of the maser, and field dependence of spin-lattice relaxation time are discussed.

The pertinent transitions and the energy level diagram of Cr³⁺ in Al₂O₃ for applied fields perpendicular to the *c* axis³ are shown in Fig. 1. For simplicity, the $\Delta M=2$ transition between

levels 1 and 3 is saturated⁴ at a pump frequency $\nu_3 = \nu_1 + \nu_2$, corresponding to a fixed dc bias field, H_0 , above any field where cross relaxation effects⁵ may occur, such as at ν_5 . The cw three-level maser⁶ would operate at $\nu_2 \ll \nu_3$, when $H = H_0$, with an inverted spin population between levels 2 and 1. If H is now increased to H_i in a time short compared to the spin-lattice relaxation time, oscillation or amplification should be obtainable at any frequency $\nu_i > \nu_2$ for which suitable maser cavity resonances occur. A gain of energy in the ratio of ν_i/ν_2 over the continuous three-level maser is obtained at the expense of energy extracted from the pulsed magnetic field. Wavelengths of about 1 mm would be generated at a field of 100 kilo-oersteds.

The maser reflection cavity, a solid rectangular parallelepiped of ruby,⁷ was designed with the two lowest modes (TE_{101} and TE_{102}) occurring at $\nu_3 = 12.61$ kMc/sec and $\nu_4 = 19.15$ kMc/sec, respectively, with undercoupled loaded cavity Q 's of about 2000 and 4800, respectively. The pump power and radiated energy were transmitted to and from the single cavity coupling iris by a tapered dielectric transition section attached to K_u -band waveguide. Both the dielectric transition and cavity were coated with a 0.001-in. silver plating in order to assure uniform penetration of the pulsed magnetic field throughout the cavity volume. The pulsed field, H_p , was generated in a solenoid (13 cm length, 7 cm i.d.) by discharge of a 2000- μ f variable voltage capacitor bank.⁸ A peak field of 9.4 kilo-oersteds was obtained at 1000 volts with a half-period of about 3 milliseconds [see Figs. 2(A), 2(B)]. The maser cavity assembly and surrounding glass Dewars were inserted in the solenoid, and the entire assembly was fixed between the pole faces of an electro-

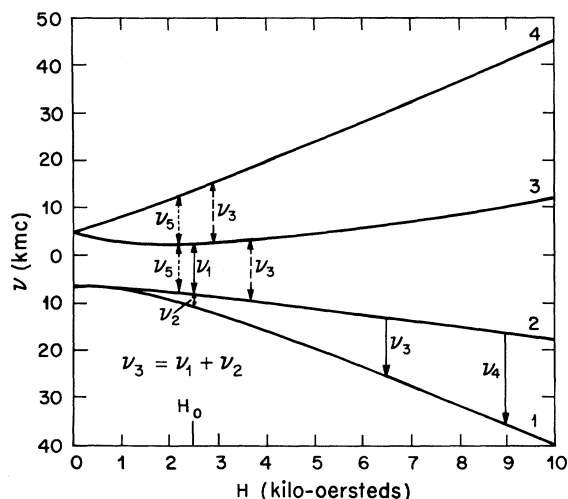


FIG. 1. Energy level diagram for Cr³⁺ in Al₂O₃ with applied field perpendicular to *c* axis. Operating points for pumping at $\nu_3 = \nu_1 + \nu_2$, and emission at ν_3 and ν_4 are indicated.