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# Variable-Temperature Infrared Spectra of $VO_2$

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The infrared spectra of $VO_2$ powder in KBr from 1300 to 400 $cm^{-1}$ during heating and cooling through the metal–insulator transition are reported. In the high-temperature metallic region, the spectra are nearly featureless, while below the transition temperature well-developed vibrational bands are observed. The spectra at room temperature before and after heating are superimposable, a result consistent with the reversibility of the metal–insulator transition. © 1987 Academic Press, Inc.

There exists a fascinating group of transition metal oxides, sometimes termed "narrowband" compounds, which undergo anomalous metal–insulator phase transitions (*1–4*). These reversible transitions tend to be accompanied by large enthalpic changes as well as manyfold changes in electrical resistivity and magnetic susceptibility. The phases often contain transition metal ions ($M$) with less than half-filled $d$-orbitals. The structures which are adopted tend to feature octahedral coordination of the metal and edge-sharing of the $MO_6$ groups—this permits direct $t_{2g}$–$t_{2g}$ orbital interactions between transition metal ions, thus enabling transitions between localized and itinerant $d$-electron behavior.

Many of the lower oxides of vanadium display metal–insulator transitions; $V_2O_3$ and $VO_2$ have been particularly well studied (*1, 5–14*). Metal–insulator phenomena occur below room temperature in the sesquioxide and at 68°C in $VO_2$. $VO_2$ displays structures derived from that of rutile. Below the transition temperature ($T_t$), homopolar $V^{4+}$ pairs form along the chains of edge-shared $VO_6$ octahedra (rutile $c$ axis); the distorted structure is monoclinic and similar to that of $MoO_2$. Above $T_t$, the pairs are broken and the $V^{4+}$ ions along the chain become equidistant; metallic conduction sets in and the tetragonal rutile-type phase is formed.

Optical absorption studies of $VO_2$ have been reported by Verleur *et al.* (*15*), Porter *et al.* (*16*), and Ladd and Paul (*17*). Barker *et al.* (*18*) reported the infrared reflectivity of crystals of $VO_2$ at three temperatures and gave a group-theoretical discussion of the infrared-active modes of the low-temperature phase. The spectrum taken above $T_t$ was essentially featureless with high reflectivity, a result which was interpreted as indicating metallic or free-carrier behavior. Perelyaev *et al.* (*19*) reported infrared spectra of a series of solid solutions $V_{1-x}Ti_xO_2$ at

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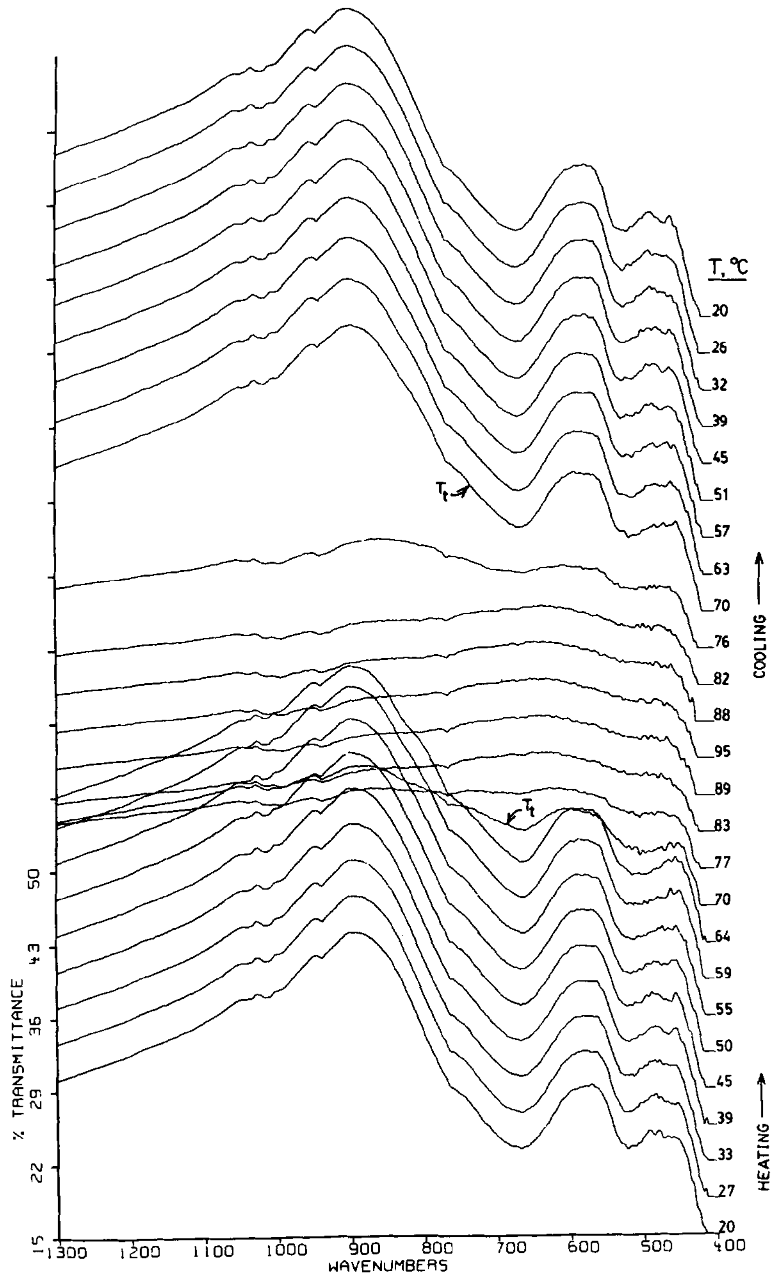

FIG. 1. Variable-temperature infrared spectra of $VO_2$ powder (spectra are successively offset by (+)3.5% T).

two temperatures; limited infrared data from doped $VO_2$ have also been reported by Heinrich *et al.* (*20*).

We report here a series of infrared spectra between 1300 and 400 $cm^{-1}$ of $VO_2$ powder during heating and cooling through the metal–insulator phase transition at 68°C. Spectra were obtained at approximately 6° intervals as the compound was heated to 100°C and then cooled to room temperature. The $VO_2$ was kindly provided by Professor B. L. Chamberland of the University of Connecticut as a granular, brilliant blue-black powder. Spectra were taken of the finely ground powder in a KBr pellet with a Nicolet Model 60 SX FTIR spectrophotometer. A high-temperature pellet transmission cell (Barnes Co.) with a temperature controller was used to obtain spectra at various temperatures.

The infrared spectra are given in Fig. 1. For clarity, the spectra have been successively offset by (+)3.5% T (one-half division). As observed by others (*18–21*), the high-temperature metallic state, stable above 68°C, is characterized by a relatively featureless infrared spectrum. The absorption bands reappear as the compound is cooled through $T_t$. After cooling, the final spectrum obtained at 20°C is essentially superimposable on the first spectrum taken at 20°C, a result consistent with a completely reversible phase transition. Temperature control and accuracy were insufficient to detect hysteresis effects. As can be seen from the spectrum at 77°C during the heating cycle, a substantial decrease in transmission is associated with the high-temperature metallic region: the transmission at 1300 $cm^{-1}$ has decreased to approximately 19% as compared to 30% at 20°C before heating.

A band model of the chemical bonding in $VO_2$ has been proposed for the semiconducting-to-metal phase transition (*22–24*). Band formation occurs because of strong metal–metal interactions among the *d*-orbitals of $t_{2g}$ symmetry, and also via strong covalent mixing of oxygen *p*-orbitals with metal *d*-orbitals. Above the transition temperature, the metal–metal band and the metal–oxygen band overlap and are each partially filled, giving rise to metallic conductivity and the tetragonal rutile structure. In the low-temperature region, vanadium–vanadium pairs form along the chains of edge-shared $VO_6$ octahedra, lowering the crystallographic symmetry to monoclinic and separating the metal–metal and metal–oxygen bands. The metal–metal band is lower in energy and becomes filled, resulting in semiconducting behavior.

It is interesting to compare the infrared profile of the metal–insulator transition in $VO_2$ with that reported recently (*3*) for the phase transition in $LiVO_2$. The transition in $LiVO_2$ near 200°C had been thought to be semiconducting–semiconducting, but the featureless and low-transmission infrared spectra obtained above $T_t$, which are very similar to those obtained here for $VO_2$, are strong indicators of metallic character in the high-temperature region. In the $\alpha$-NaFe $O_2$-type structure of $LiVO_2$, the trivalent vanadium ($d^2$) ions are confined to hexagonal close-packed-like planes; each $V^{3+}$, therefore, has six nearest $V^{3+}$ neighbors. The vanadium–vanadium separation suggests that strong metal–metal interactions are possible within the planes, and it was suggested (*3*) that the metal–insulator transition is two dimensional, with a symmetrical vanadium metal-cluster-layer forming in the low-temperature region. Electrical resistivity studies on powders, which had indicated semiconducting behavior both below and above $T_t$, are therefore misleading. The similarity, however, of the infrared profile of the transition in $LiVO_2$ to that of the known metal–insulator transition in $VO_2$ indicates that $LiVO_2$ is also metallic in its high-temperature region.

## References

*1.* J. B. GOODENOUGH, "Magnetism and the Chemical Bond," and references cited therein. Interscience, New York (1963).

*2.* J. SPALEK, A. DATTA, AND J. M. HONIG, *Phys. Rev. B* **33**, 4891 (1986).

3. T. A. Hewston and B. L. Chamberland, *J. Solid State Chem.* **65,** 100 (1986).
4. D. Adler, *Rev. Mod. Phys.* **40,** 714 (1968).
5. P. Hertel and J. Appel, *Phys. Rev. B* **33,** 2098 (1986), and references cited therein.
6. C. B. Greenberg, *Thin Solid Films* **110,** 73 (1983), and references cited therein.
7. B. L. Chamberland, *J. Solid State Chem.* **7,** 377 (1973).
8. G. J. Hyland, *Proc. Phys. Soc. C* **1,** 189 (1968).
9. J. B. Goodenough, *J. Solid State Chem.* **3,** 490 (1971).
10. P. F. Bongers, *Solid State Commun.* **3,** 275 (1965).
11. T. M. Rice and D. B. McWhan, *IBM J. Res. Dev.* **14,** 251 (1970).
12. J. B. MacChesney and H. J. Guggenheim, *J. Phys. Chem. Solids* **30,** 225 (1969).
13. P. J. Fillingham, *J. Appl. Phys.* **38,** 4823 (1967).
14. T. Mitsuishi, *Japan J. Appl. Phys.* **6,** 1060 (1967).
15. H. W. Verleur, A. S. Barker, Jr., and C. N. Berglund, *Phys. Rev.* **172,** 788 (1968).
16. V. R. Porter, W. B. White, and R. Roy, *J. Solid State Chem.* **4,** 250 (1972).
17. L. A. Ladd and W. Paul, *Solid State Commun.* **7,** 425 (1969).
18. A. S. Barker, H. W. Verleur, and H. J. Guggenheim, *Phys. Rev. Lett.* **17,** 1286 (1966).
19. V. A. Perelyaev, V. I. Miller, L. A. Perelyaev, N. E. Grebenshchikova, G. P. Shveikin, S. I. Alyamovskii, *Russ. J. Inorg. Chem.* **25,** 1749 (1980).
20. A. Heinrich, E. T. Terukov, W. Reichelt, H. Wagner, and H. Oppermann, *Phys. Status Solidi* **72,** K61 (1982).
21. P. Ganguly and N. Y. Vasanthacharya, *J. Solid State Chem.* **61,** 164 (1986).
22. M. L. Gray, W. J. Croft, K. Dwight, and A. Wold, *J. Solid State Chem.* **54,** 421 (1984).
23. J. B. Goodenough, *Bull. Chem. Soc. Fr.* **4,** 1200 (1965).
24. D. B. Rogers, R. D. Shannon, A. W. Sleight, and J. L. Gillson, *Inorg. Chem.* **8,** 841 (1969).