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RAMAN SCATTERING AND METAL-INSULATOR TRANSITION IN $(V_{1-x}Cr_x)_2O_3$ $(0 \le x \lesssim 0.03)$*

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Metal-insulator transitions in $(V_{1-x}Cr_x)_2O_3$ with $x \lesssim 0.03$ have been studied by Raman scattering. The effects of Cr-doping on the Raman lines due to phonons in the temperature range of the so called high temperature transition may be explained by the two-bands model proposed by Zeiger. As regards the M-AFI and the I-AFI transitions, the Raman measurements show that the electrical transition is not a highly important factor for the lattice transition. The effects of a magnetic field B=100 kG on the scattering in V_2O_3 are also reported.

I. Introduction

The crystals V_2O_3 and $(V_{1-x}Cr_x)_2O_3$ have received a great deal of attention in recent years. Various properties have been investigated as function of temperature and pressure for various contents, x's of Cr. In the case of V_2O_3, as the temperature is decreased at atmospheric pressure, the low metalic electrical resistivity increases abruptly by many order of magnitude at ~150 K[1,2], simultaneously, the crystal changes from α-corumdum to monoclinic structure[3], and the antiferromagnetic ordering in the crystal occures[4]. The transition temperature will be denoted by T_1. It is usually said that the crystal is in the M-phase at $T>T_1$ and in the AFI-phase at $T<T_1$. By doping a small content of Cr, the electrical resistivity increases by several orders at room temperature[5]. The resistivity in the crystal with $x \lesssim 0.014$ shows abrupt decrease at T_2 with decreasing temperature, and again increases abruptly as the temperature reaches a lower value T_1. The change of resistivity at T_2 is smaller in magnitude than the change at T_1. The crystal is said to be in I-phase at $T>T_2$, in M-phase at $T_1<T<T_2$ and in AFI-phase at $T<T_1$. With increasing x, T_2 decreases and T_1 increases somewhat. For a sufficiently large x, the resistivity no longer shows a trough[5], and the resistivity and the magnetic susceptibility vary with temperature rather smoothly at around T_1[6].

The transition between I- and M-phase is not accompanied with the crystallographic change and magnetic ordering, and Rice et al.[7] and Brinkman and Rice[8] have interpreted it as a Mott-transition. Zeiger, on the other hand, has showed that many physical properties of the metal-insulator transition in Ti_2O_3 and of the high temperature transition in V_2O_3 and $(V_{1-x}Cr_x)_2O_3$ were explained in terms of the band crossing model based on a Hartree-Fock free energy calculation including electron-electron Coulomb energy, elastic energy and band-electron entropy without a Mott-transition[9]. In the case of M-AFI transition, the three properties,electrical resistivity, structure and magnetic nature change at the same temperature. Castellani et al.[10] have suggested that the lattice distortion is purely magnetostrictive and of no direct importance to the transition mechanism.

The purpose of the present work is to study the interrelationship of the three properties in the transition by Raman scattering. The effects of an applied magnetic field on the scattering have also been investigeted to some extent.

II. Experimental Procedure

The details of the experimental procedure have been reported elsewhere[11]. The samples were cut from the single crystals grown by the Czochralski method in the Read-Triarc furnace in the Central Materials Preperation Facility of Purdue University. The scattering surface was normal to the hexagonal three-fold rotation axis C_3 which is taken to be the coordinate axis Z. The plane of incidence of the 4880 A line of an argon-ion laser in the measurement was perpendicular to a C_2 axis in the hexagonal basal plane, which is taken to be coordinate axis X. The angle of incidence in the measurement was $(\vec{k}_I, \vec{Z})=70^\circ$. The refraction of laser and the scattered beams at the sample surface is determined by the refractive index n=1.76 of the material. It follows that, in terms of the chosen coordinate axes, $\vec{E}_I(0,-0.85,0.53)$. When the analyzer was used in the scattered beam, we had $\vec{E}_s(0,0.98,0.19)$ for $\vec{E}_s^\circ \parallel \vec{E}_I^\circ$, and $\vec{E}_s(-1,0,0)$ for $\vec{E}_s^\circ \perp \vec{E}_I^\circ$.

III. Results and Discussions

Figure 1 shows the measured spectra for the M-phase of V_2O_3 and the I-phase of $(V_{0.985}Cr_{0.015})_2O_3$. The phonon modes of five of the peaks of V_2O_3 have been identified by previous work[12]. One extra, weak peak was observed at $\Delta\nu \sim 327$ cm^{-1}. Seven Raman active modes are expected for the α-corundum structure, two A_{1g} modes and five E_g modes[13]. Two A_{1g} modes and three E_g modes having been identified, the extra peak should be associated with an E_g mode. The spectra of the Cr-doped V_2O_3 are similar to those of pure V_2O_3. It shows that Cr-doping does not change the crystal structure. The phonon modes associated with the peaks may be taken to be those associated with the peaks of pure V_2O_3, which are close in frequency shifts, respectively.

The frequency shifts Δν's of the scattering peaks are listed in Table I. Cr-doping increased Δν by several cm^{-1}, with the exception of one E_g peak, the $\Delta\nu \sim 210$ cm^{-1} of which was not changed appreciably.

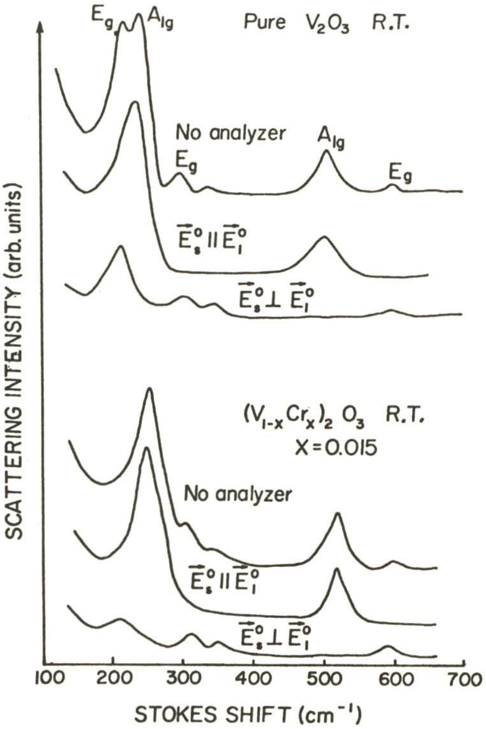

Fig.1 Raman spectra of V_2O_3 in M-phase and of $(V_{0.985}O_{0.015})_2O_3$ for the I-phase: The intensity of E_g(210 cm^{-1}) is much weaker in Cr-doped sample than in V_2O_3

Table 1 The effect of Cr ($x \lesssim 0.03$) doping on the frequency shifts in cm^{-1} and the scattering intensities at R.T. for each phonon mode: $\Delta\nu$ denotes the frequency for V_2O_3

	$\Delta\nu$	$\Delta\nu(Cr)-\Delta\nu$	I(Cr)/I(0)
E_g	210	~0	<0.2
A_{1g}	234	15	1
E_g	296	10	1
E_g	327	10	1
A_{1g}	501	15	2
E_g	595	5	1

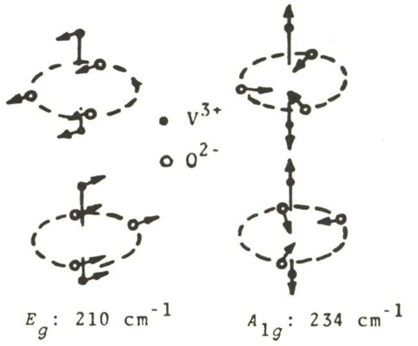

Fig.2 Two vibration modes of atoms in the unit cell of α-corundum structure

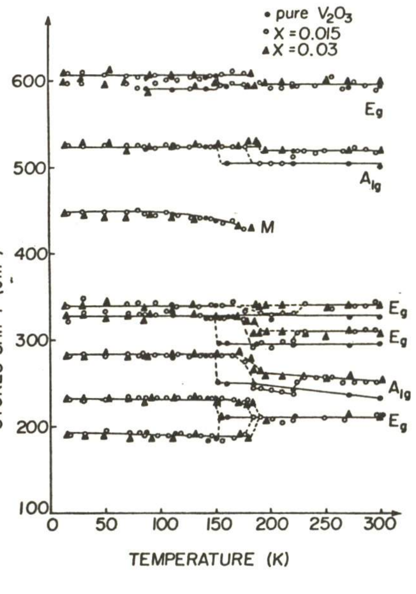

Fig.3 Temperature dependence of $\Delta\nu$ for each Raman line

The results may be due to the effect of Cr-doping on the lattice dimension[5]. There are two molecules in a primitive cell of α-corundum structure. As shown in Fig.2, of the seven Raman active modes, one E_g mode corresponds to a vibration purely perpendicular to the c-axis. For this mode of vibration, the restoring force may not be significantly affected by the change of c while the other modes of vibration do show some stiffening reflected in a noticeable increase of $\Delta\nu$. So, the E_g line at $\Delta\nu=210$ cm^{-1} is identified to be this mode of vibration.

The spectra in Fig.1 show that the intensity of the E_g (210 cm^{-1}) is considerably weaker in Cr-doped V_2O_3 than in V_2O_3. The same situation has also occured at the transition from I- to M-phase with decreasing temperature in $(V_{0.985}Cr_{0.015})_2O_3$. The intensity of the E_g (210 cm^{-1}) line increased abruptly as the temperature crossed T_2~223 K of the I-M transition. In a model used by Zeiger[9,14] to treat the high temperature transition in V_2O_3 and $(V_{1-x}Cr_x)_2O_3$ and the transition in Ti_2O_3, the electrons in two energy bands, 1 and 2, are considered. The orbitals in band-1 are elongated along the c-axis, and the orbitals in band-2 are spread more out in the basal plane. Properties of material are related to the division of the available electrons between two bands. Electrons more spread out in the basal plane are more important for ion vibration in the basal plane. The result that the E_g (210 cm^{-1}) peak is weaker in the I-phase than in the M-phase may be an indication that the electron in band-2 is smaller in I-phase.

Figure 3 shows the temperature dependence for each phonon line. In the case of the 3 at.% Cr sample, the resistivity did not show sharp transition in passing from I-phase to AFI-phase[11]. On the other hand, Fig.3 shows that the frequency shifts of the 3% sample remained essencially constant as T was decreased to 181 K, where the scattering spectrum changed abruptly as in the case of V_2O_3 at the M-AFI transition.

Figure 4 is the comparison between experiment and theoretical result

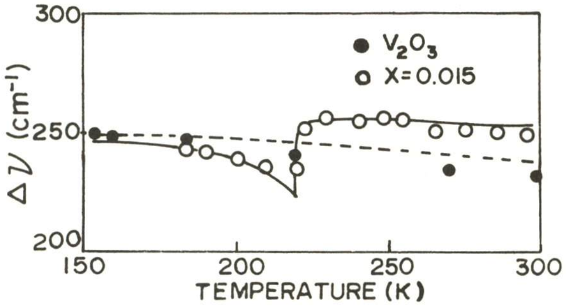

Fig.4 Comparison of Experiment (○ and ●) with theory by Zeiger(— and ---) for lower frequency A_{1g} mode

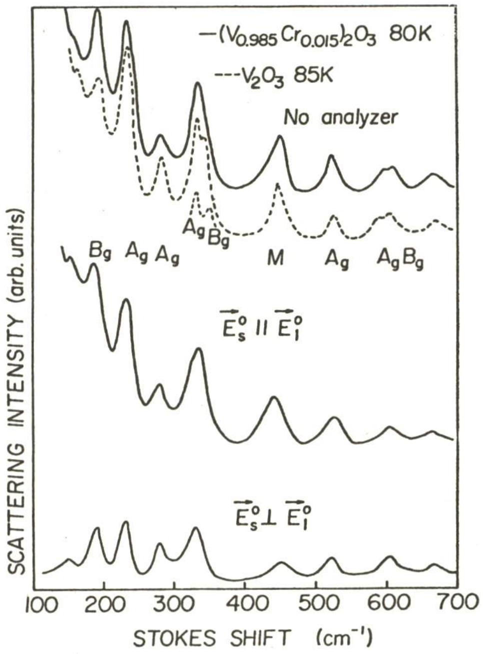

Fig.5 Raman spectra in AFI-phase

calculated by Zeiger's model for the temperature dependence of the frequency shift of A_{1g} mode with lower energy. For the fitting, the correlation energy parameter κ[14] was 9.9 for $(V_{0.985}Cr_{0.015})_2O_3$, and was 10.05 for V_2O_3. The agreement between experiment and theory is fairly good. The vibration of atoms corresponding to this A_{1g} mode is shown in Fig.2.

Figure 5 shows the Raman spectra in AFI-phase, where M denotes an antiferro magnon scattering[12].

Some investigations were made on the effect of B=100 kG. The used scattering geometry gave three possible angles between B and magnetic moment M, 0°, 56° and 70° [11] in AFI-phase according to the antiferromagnetic alignment[4]. An applied magnetic field up to 100 kG did not produce an observable effect on the resistance of a sample. One observed effect of 100 kG on the scattering is a small increase in $\Delta\nu$, by $\sim$10 cm^{-1} of the magnon line M, without an appreciable change in the $\Delta\nu$'s of phonon lines at 150 K. Another effect was that the magnitude of the $\Delta\nu\sim$160 cm^{-1} line was appreciably reduced without a significant change in the relative magnitude of phonon lines.

These results show that magnetic interactions do not seem to be dominant factor for electrical transition and that the desirability of more extensive investigation on the effect of an applied magnetic field.

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1) M.Föex: Compt. Rend. 223(1946) 1126.
2) J.F.Morin: Phys. Rev. Letters 3(1959) 34.
3) P.D.Dernier: J. Phys. Chem. Solids 31(1970) 2569.
4) R.M.Moon: Phys. Rev. Letters 25(1970) 527.
5) D.B.McWhan and J.P.Remeika: Phys. Rev. B2(1970) 3734.
6) A.Menth and P.J.Remeika: Phys. Rev. B2(1970) 3756.
7) T.M.Rice,D.B.McWhan and W.F.Brinkman: *Proceeding of the 10th Inter. Conf. on Physics of Semiconductors(1970)* 293.
8) W.F.Brinkman and T.M.Rice: Phys. Rev. B2(1970) 1324.
9) H.J.Zeiger: Phys. Rev. B11(1975) 5132.
10) C.Castellani,C.R.Natoli and J.Ranninger: Phys.Rev.B18(1978) 4967.
11) C.Tatsuyama and H.Y.Fan: Phys. Rev. B21(1980) 2977.
12) N.Kuroda and H.Y.Fan: Phys. Rev. B16(1977) 5003.
13) A.S.Barker,Jr.: Phys. Rev. 132(1968) 1474.
14) H.J.Zeiger: *Lincoln Laboratory Technical Report*(MIT, 1974).