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Lattice Dynamics of WO_3

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The Raman spectrum of WO_3 has been investigated from −180 to 290°C. An interpretation of the phonon spectra of the phases with higher symmetries is carried out by group theory. The normal coordinates of tetragonal WO_3 have been calculated and a correlation of the phase transitions with the critical behaviour of some of the normal modes has been attempted.

Introduction

WO_3 exhibits a perovskite-like structure and shows five phase transitions between −180 and 900°C. During cooling, the symmetry changes from tetragonal to orthorhombic and then to monoclinic. Even a triclinic modification is known. The space groups found by Kehl, Hay & Wahl (1952), Salje & Viswanathan (1975), and Tanisaki (1960) are D^7_{4h}–$P4/nmm$, D^{16}_{2h}–$Pmnb$, and C^5_{2h}–$P2_1/n$. Some of the transformations take place very rapidly and it is possible to talk of a structural 'collapse' at such transition points. As the transformation mechanism has been investigated by other methods (Salje & Viswanathan, 1975), it is now possible to present the results of the study of the lattice dynamics of WO_3.

Experimental

WO_3 crystals were studied by Raman spectroscopy from −180 to 290°C. In addition the spectrum was recorded at room temperature. The samples used have been described earlier (Salje & Viswanathan, 1975) and consisted of monoclinic and triclinic crystals. The latter were without any optical domain structure and hence measurements could be made with polarized light. But the crystals were so small (approximately $0{\cdot}5\times0{\cdot}5\times0{\cdot}1$ mm) that the Raman tensors could be determined only approximately. The maximum value of the anisotropy which could be obtained by this method amounts to 20%. In some cases it was only 5%. The scattering coefficient that could be considered characteristic was d_{zz}. The Raman lines which indicate this polarization are indexed with Z in Fig. 1. The spectra, shown in Fig. 2, were obtained on heating and then on cooling the crystals to the temperature of liquid nitrogen. It can be seen that there is a quasi-continuous shift of the Raman lines with increase of temperature above the lowest transition point. At this phase transition, the Raman spectrum shows a complete change in both the monoclinic and the triclinic modifications. The changes are shown in Fig. 3 which illustrates the dependence of the individual phonon frequencies on the temperature.

A comparison of the Raman and infrared spectra (Fig. 4) reveals that it is almost impossible to follow the critical phonon lines by infrared spectroscopy. However, the infrared-spectra can give indications of the selection rules for the room-temperature phase.

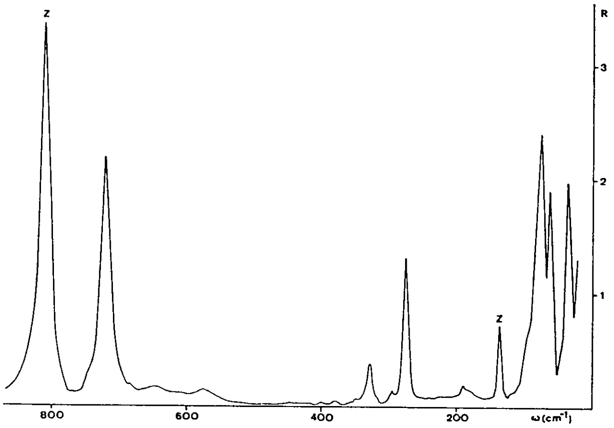

Fig. 1. Raman spectrum of WO_3.

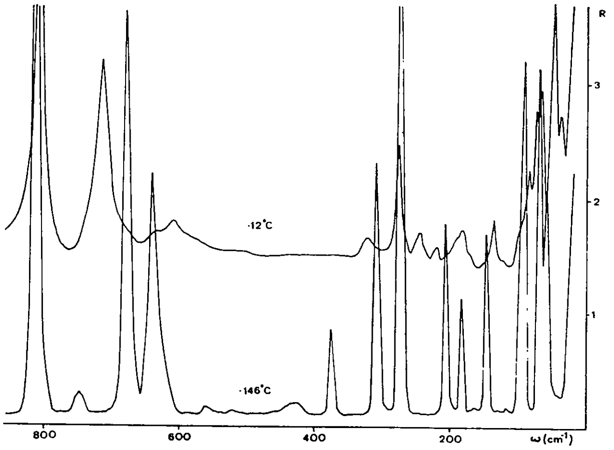

Fig. 2. The effect of temperature on the Raman spectrum of WO_3.

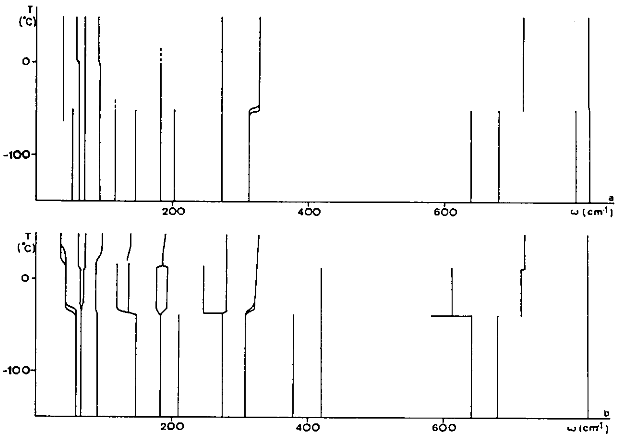

Fig. 3. The dependence of the phonon frequencies on temperature for the monoclinic (*a*) and triclinic (*b*) modifications.

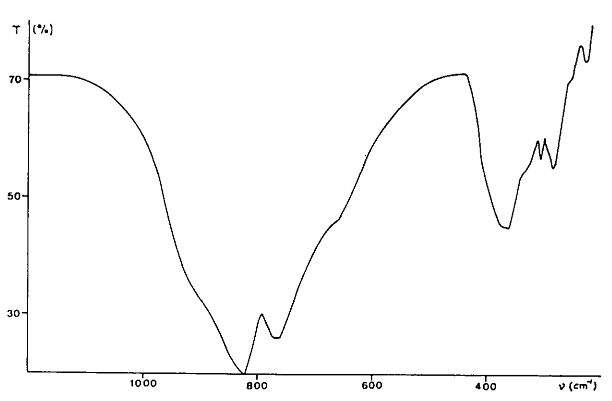

Fig. 4. Infrared spectrum of WO_3.

Calculation of the normal coordinates for the tetragonal phase

In order to interpret the phonon spectra and understand the phase transitions, it is first helpful to analyse the Γ phonons ($k=0$) responsible for the Raman spectrum and to study, theoretically, the critical phonons typical for the different structural distortions. Hence the normal coordinates were calculated for the phase with the highest symmetry.

The ideal perovskite structure is cubic, space group O_h^1–$Pm3m$. The corresponding representations are

$$\Gamma=4T_{1u}+T_{2u}\,.$$

The normal coordinates were calculated by Salje (1973). Even at the highest temperature, WO_3 does not show this symmetry. Nevertheless the real structure of the highest-symmetry phase can be correlated with a hypothetical transition O_h^1–D_{4h}^7. This transition is characterized by a soft-mode behaviour of a critical mode with a wavelength $\sqrt{2}a$ and a direction of propagation [110]. This means, that the M point in the Brillouin zone of the cubic phase shows a critical behaviour and becomes a Γ point in the tetragonal phase. The total number of phonons is thus increased. Simultaneously the lowering of the symmetry reduces the multiplicity of the $\Gamma(O_h^1)$ representations.

The calculations, based on the theory of representations, give the following rules for the splitting:

$$\Gamma=A_{1u}+4A_{2u}+2B_{1u}+B_{2u}+5E_u+2A_{1g}+2E_g$$

where A_g and E_g represent the Raman-active phonons. The method of Bagavantham & Venkatarayudu (1969) was followed to calculate the normal coordinates of the representations. The character table is given in Table 1

Table 1. *Character table of space group* D_{4h}^7

	E	C_4	C_2	C_4^3	$2U_d$	$2U$	I	S_4	S_4^3	$2\sigma_v$	$2\sigma_d$	σ_h
A_{1u}	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1
A_{2u}	1	1	1	1	−1	−1	−1	−1	−1	1	1	−1
B_{1u}	1	−1	1	−1	−1	−1	−1	1	1	−1	1	−1
B_{2u}	1	−1	1	−1	1	1	−1	1	1	1	−1	−1
E_u	2	0	−2	0	0	0	−2	0	0	0	0	−2
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
E_g	2	0	−2	0	0	0	2	0	0	0	0	−2

Table 2. *Normal coordinates for* Γ *phonons in* D_{4h}^7

Mode	Eigenvectors (not normalized)
2 A_{1g}	$z(W_1)-z(W_2),\ z(O_5)-z(O_6)$
2 E_g	$x(W_1)-x(W_2),\ y(W_1)-y(W_2),\ x(O_5)-x(O_6),\ y(O_5)-y(O_6)$
1 A_{1u}	$[x(O_1)+y(O_1)]-[x(O_2)-y(O_2)]-[x(O_3)+y(O_3)]+[x(O_4)-y(O_4)]$
4 A_{2u}	$z(W_1)+z(W_2),\ z(O_5)+z(O_6),\ \sum z_i=\text{translation}$ $x(O_1)+x(O_2)-x(O_3)-x(O_4)-y(O_1)+y(O_2)+y(O_3)-y(O_4)$
2 B_{1u}	$x(O_1)-x(O_2)-x(O_3)+x(O_4)-y(O_1)-y(O_2)+y(O_3)+y(O_4)$ $z(O_1)-z(O_2)+z(O_3)-z(O_4)$
1 B_{2u}	$x(O_1)+x(O_2)-x(O_3)-x(O_4)+y(O_1)-y(O_2)-y(O_3)+y(O_4)$
5 E_u	$x(W_1)+x(W_2),\ y(W_1)+y(W_2),\ x(O_5)+x(O_6),\ y(O_5)+y(O_6)$ $x(O_1)+x(O_3),\ x(O_2)+x(O_4),\ y(O_1)+y(O_3),\ y(O_2)+y(O_4)$ $z(O_1)+z(O_3),\ z(O_2)+z(O_4)$

and the normal coordinates are summarized in Table 2. In Fig. 5 these normal coordinates are shown graphically. The critical mode is A_{1g} with the coordinates $z(W_1)-z(W_2)$. This mode would correspond to the M point in a hypothetical cubic phase, but it appears as Γ phonon in space group D_{4h}^7.

The influence of the phase transitions

The phonons, estimated for the tetragonal symmetry, are closely correlated with the phonon spectra of the orthorhombic and monoclinic phases. Unfortunately, the available data on the structure of monoclinic WO$_3$ at room temperature are conflicting. Moreover, a structure determination of the orthorhombic phase has not yet been carried out. If it is assumed that the values given by Loopstra & Boldrini (1966) are correct, it can be concluded that the cause of the structural distortion lies in the critical behaviour of a phonon in the X point of the tetragonal Brillouin zone (Zak, 1969). This would cause an additional zigzag movement of the W positions. Hence, on theoretical grounds, it can be expected that the space group of the orthorhombic phase will be D_{2h}^x.

During the transition to the room-temperature phase, the symmetry is further lowered to C_{2h}^5, which must be attributed to rotations of the oxygen octahedra. This deformation of the structure is in fact characteristic of all perovskites with small A atoms.

The irreducible representations of the monoclinic space group are

$$\Gamma=24(A_g+B_g+A_u+B_u)\,, \quad \Gamma_{\text{trans}}=A_u+2B_u\,.$$

Hence 48 Raman lines can be expected. In addition, 45 absorption peaks should be observed in the infrared spectrum. The frequencies of both sets of phonon signals should be different because of the defined parity of the representations. The expected Raman tensors are:

$$A_g=\begin{pmatrix} a & 0 & a \\ 0 & b & 0 \\ d & 0 & c \end{pmatrix} \quad \text{and} \quad B_g=\begin{pmatrix} 0 & e & 0 \\ e & 0 & f \\ 0 & f & 0 \end{pmatrix}.$$

The d_{zz} polarization of the Raman lines is therefore due to A_g phonons. The experimental values of phonon frequencies are listed in Table 3.

Table 3. *Experimental values of the frequencies of Γ phonons*

ω (cm^{-1})	Parity	Polarization	ω (cm^{-1})	Parity	Polarization
33	Raman	d_{zz}	330	Raman	–
60	Raman	–	335	Infrared	–
73	Raman	–	370	Infrared	–
93	Raman	–	665	Infrared	–
133	Raman	d_{zz}	719	Raman	d_{zz}
230	Infrared	–	765	Infrared	–
275	Raman	–	808	Raman	d_{zz}
285	Infrared	–	825	Infrared	–
310	Infrared	–	920	Infrared	–

A direct observation of the phase transitions in the low-temperature region is possible by Raman spectroscopy. The measured frequencies of the lowest-energy transversal phonon in the temperature range from 20 to 290 °C are shown in Fig. 6. The temperature frequency relation follows exactly the Curie–Weiss law

$$\omega \simeq \sqrt{T-T_c}\,.$$

An extrapolation gives the value of 750 °C for T_c. This is approximately the transition temperature to the tetragonal phase. However, experiments at higher temperatures are not possible because of the low-energy shift of the optical absorption edge (Salje, 1974*a*).

The triclinic modification shows a drastic change in its electrical properties at −27 °C and the same has been observed at −52 °C for the monoclinic variety (Salje & Viswanathan, 1975). A corresponding change in the Raman spectra is seen in Fig. 3, which cannot been explained on the basis of parity changes. The im-

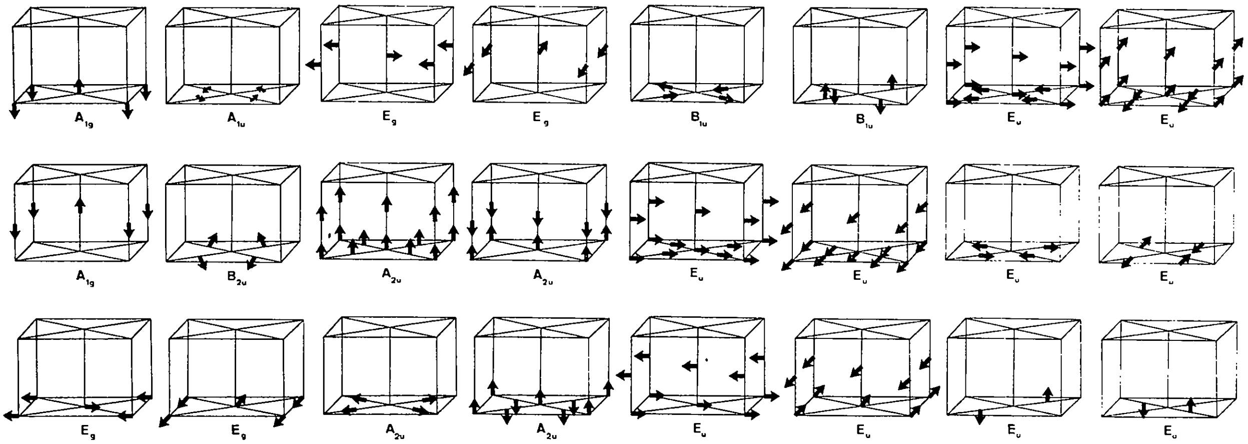

Fig. 5. Normal coordinates of tetragonal WO$_3$.

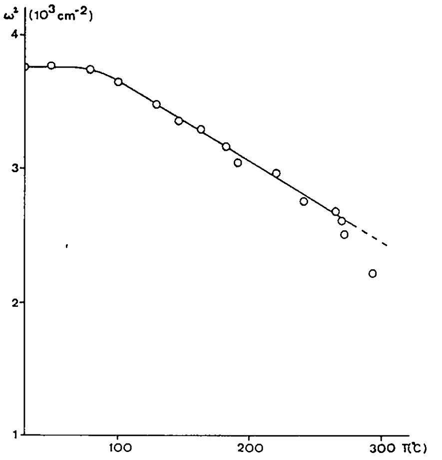

Fig. 6. Curie–Weiss behaviour of the lowest transverse phonon in WO₃.

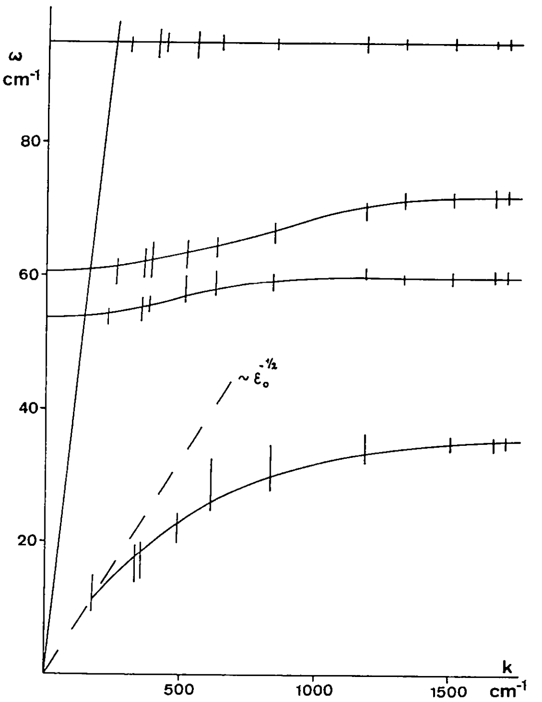

Fig. 7. Polariton dispersion curve of triclinic WO₃.

plied changes in the bonding relations should be accompanied by an additional distortion in the structure. WO_3 is actually piezoelectric at low temperatures and hence, in contrast to the high-temperature phases, does not possess an inversion centre. Experimentally no discontinuities in the lattice constants were observed by Salje & Viswanathan (1975). These observations are contrary to the results of Tanisaki (1960). Therefore, an interpretation of the Raman spectra of the low-temperature phase is not possible without a knowledge of the correct structure.

Determination of the polariton dispersion in triclinic WO_3

WO_3 shows polar electrical properties at low temperatures. According to Le Bihan & Vacherand (1970) the crystals are ferroelectric in this phase. The values of the dielectric constants are quite high. At higher temperatures, the structure becomes 'antiferroelectric', but no measurements of electrical hysteresis loops can be made because of the high electrical conductivity. Burstein (1969) has described a spectroscopic method to determine the electrical susceptibility of $BaTiO_3$. This takes advantage of the fact that the polariton dispersion of the lowest transverse mode possesses a slope

$$\frac{d\omega}{dk} = \frac{c}{\sqrt{\varepsilon}}\,.$$

A procedure for measuring the polariton dispersion has already been described (Salje, 1974*b*). A similar procedure was used for WO_3. The wave vector of the polariton examined was parallel to [001]. The measured frequencies are shown in Fig. 7. It follows that only the phonons with frequencies near 35, 60 and 72 cm^{-1} are transverse in character. In the polariton range, the frequency of the lowest transverse mode decreases compared to the origin of the Brillouin zone. The gradient at this point was found by extrapolation, the related dielectric constant being 230. The magnitude of this value is in accordance with the strong dielectric polarizability in the piezoelectric phase of WO_3.

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