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Physical Properties and Phase Transitions in WO_3

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A study of the phase transitions in WO_3 crystals by Raman and absorption spectroscopy reveals that WO_3 possesses two stable (or metastable) modifications at room temperature, differing slightly but definitely in their physical properties. Measurements of electrical conductivity show that both are insulators at low temperatures and semiconductors at higher temperatures. One is monoclinic and the other triclinic. Both exhibit at lower temperatures discontinuities in their physical properties without accompanying changes in cell parameters.

Ever since Bräkken (1931) found that WO_3 has a perovskite-like structure, many authors have investigated it by different methods with a view to understanding its physical properties. These crystals became all the more interesting after it was shown that WO_3 exhibits a large non-linear electrooptic effect (Salje, 1974). The structure refinements carried out by Tanisaki (1960*a*) and Loopstra & Boldrini (1966) indicate that the structure of WO_3 shows considerable deviations from the ideal perovskite type, the distortions corresponding to 'antiferroelectric' displacements of the W atoms and mutual rotations of the oxygen octahedra. As in most of the substances with perovskite-like structure, the type and the magnitude of the distortions are found to be dependent on temperature.

On the basis of anomalies in the thermal and electrical properties (Sawada, 1956; Foex, 1945, 1949) it was concluded that there should be changes in the structure of WO_3 at about −50, −20, 330, 740, 910 and 1230°C. The X-ray data (Wyart & Foex, 1951) showed that WO_3 becomes orthorhombic above 330°C and tetragonal above 740°C. Tanisaki (1960*b*) claims to have observed by X-ray analysis a triclinic modification below 10°C and a monoclinic one below −40°C. Hence it was assumed that all the discontinuities in the electrical resistivity or specific heat could be correlated with corresponding crystallographic transformations. However, during a preliminary study of the properties of WO_3 certain discrepancies between our results and the literature data were noted. Hence it was thought desirable to study WO_3 systematically by different physical methods including X-ray analysis, with the same specimen for all experiments. It was hoped that it would not only explain some of the discrepancies in the reported data, but also help us to understand the nature of the different transitions.

Preparation of samples

To prepare crystals of WO_3 a pure sample of powdered material (Merck Nr. 829) was tempered at 800°C in a closed Pt crucible for about 100 h. The tempered sample was then heated to 1525°C, held at this temperature for two hours, and then cooled to 1200°C at a rate of 50°C/hour. After this treatment, two kinds of product were recovered from the crucible. One of them (I) is the main recrystallized molten mass. The other (II) consists of small crystals with an approximate size $0{\cdot}2\times0{\cdot}2\times0{\cdot}005$ mm, which were found sticking to the walls of the crucible and the surface of the molten mass. Only these crystals were optically clear and free of any domain structure. They are thought to have

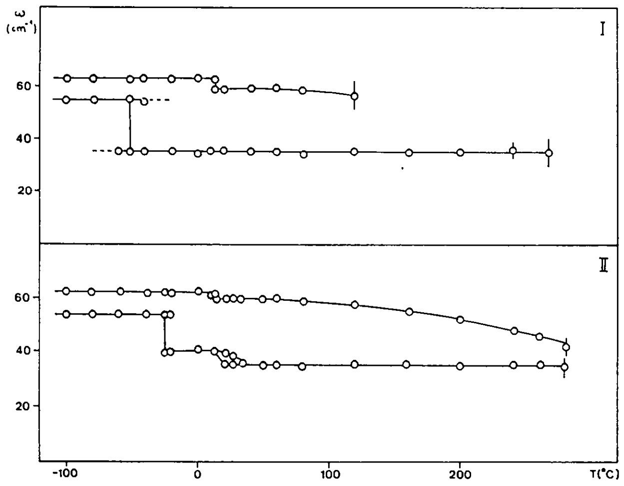

Fig. 1. The temperature dependence of the low-frequency optical phonons for WO_3(I) and WO_3(II).

Table 1. *Cell dimensions of the different* WO_3 *modifications*

		a (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	Volume (Å³)
	WO_3 (I)	7·302 (2)	7·530 (2)	3·846 (1)	90·00	90·88 (2)	90·00	211·4 (1)
	WO_3 (II)	7·304 (3)	7·514 (3)	3·844 (1)	88·86 (3)	90·84 (3)	90·94 (3)	210·9 (1)
Orthorhombic	WO_3 (480°C)	7·341 (4)	7·570 (4)	3·877 (2)	90·00	90·00	90·00	215·4 (2)
Tetragonal	WO_3 (740°C)	5·191 (2)	5·191 (2)	3·858 (1)	90·00	90·00	90·00	103·9 (1)

been formed by sublimation. Subsequent X-ray examination has shown that (I) has monoclinic symmetry and (II) is triclinic with lattice constants given in Table 1. The lattice parameters are identical to those obtained by Tanisaki (1960*b*) and Roth & Warring (1966). It has been observed for the first time that both modifications can form simultaneously. Thus it was difficult to get a pure sample of only one variety.

Methods of examination

(1) *Raman spectroscopy*

Raman spectroscopy has been used to determine the transition temperatures of WO_3. Hitherto optical, electrical or X-ray methods have been applied. It is found that Raman spectroscopy is the most sensitive technique for distinguishing the individual thermodynamic phases. For example, Fig. 1 shows the dependence of low-frequency phonons of both (I) and (II) on temperature. The transition temperatures are listed in Table 2. These values were determined as the temperature was raised. A hysteresis in temperature up to 37 °C has been observed in the temperature range studied.

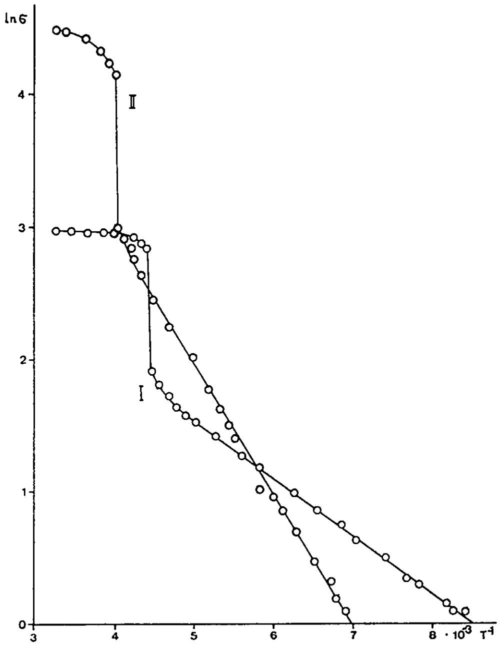

Fig. 2. Arrhenius plot of the electrical conductivity for both modifications.

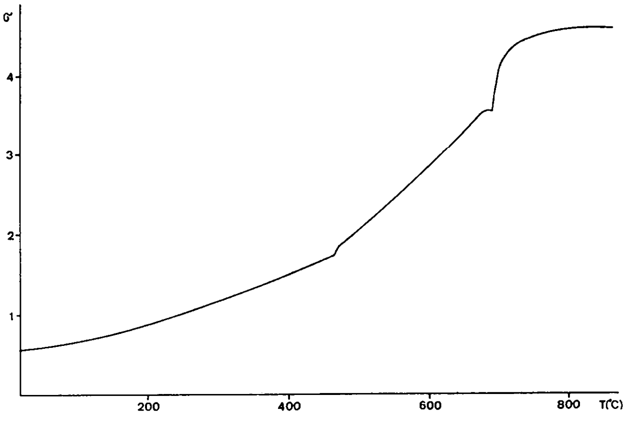

Fig. 3. Variation of the electrical conductivity with temperature (above 20 °C) for WO_3(I).

Table 2. *Temperatures of the reversible phase transformations*

WO_3(I)	−52 °C	17 °C	467 °C	680 °C
WO_3(II)*	−27 °C	7–29 °C		

* WO_3(II) is unstable above approximately 200 °C and transforms irreversibly to the monoclinic variety.

It is noteworthy that the rate of transformation during the transition at −52 °C [−27 °C for (II)] is considerable. Both modifications are completely transformed within an interval of 0·05 °C, if the temperature is increased at the rate of 20 °C/h. Though the other transformations do not take place so rapidly, the largest interval in temperature is still found to be 0·5 °C. The only exception is the one at 290 °C which shows a broad interval (Salje, 1974). The transitions at higher temperatures could not be determined by Raman spectroscopy as the lines became too weak.

(2) *Specific resistivity*

The two modifications behave differently as regards their electrical conductivities. Measurements made on the low-temperature phase [below −52 °C for (I) and below 27 °C for (II)] give a curve (Fig. 2), which indicates a relationship $\sigma=\sigma_0\mathrm{e}\ \mathrm{xp}(-E/kT)$ with an activation energy E. The scale factor σ_0 is so small that this behaviour cannot be due to impurity semiconduction. On the other hand, there is a sudden, 30-fold increase in the conductivity from −52 °C, whereby σ_0 assumes the values of a semiconductor.

Table 3. *Experimental values of the scale factor,* ln σ_0, *the formation energy E and the transition temperature,* T_{trans}

	ln σ_0	E (eV)	T_{trans} (°C)
WO_3(I)	0·92	0·085	−52
WO_3(II)	1·14	0·17	−27

The calculated values of E and ln σ_0 are listed in Table 3. When the temperature was increased further, a negative coefficient was observed for electrical conductivity. The measurements shown in Fig. 3 were made on polycrystalline material and the transition temperatures thus measured are given in Table 2. In general the observed temperatures may strongly depend on the previous history of the crystals.

(3) *Absorption spectra*

In order to investigate further the band structure of WO_3, optical measurements were carried out near the fundamental edge. The colour of WO_3 was first determined at room temperature. Fig. 4 shows the absorption spectrum of WO_3 with the fundamental edge at 2·58 eV, which value was found to be the same for both modifications.

The sample was then cooled to $-196\,^\circ$C and slowly heated. During the process of heating, the absorption spectra shown in Fig. 4 were obtained. It can be seen that the spectrum of the low-temperature phase remains practically unaffected, but the spectrum shows a sudden change at the transition point. Salje (1974) has investigated the spectrum at high temperatures and observed a less striking discontinuity at 290 °C.

These measurements indicate that only at temperatures above $-52\,^\circ$C is the typical band structure of semiconductors present with an absorption edge in the visible region. This is in agreement with the behaviour of the electrical conductivity. For comparison, transition temperatures were also determined by absorption spectroscopy (Fig. 5) with thin crystals of WO_3 and a constant photon energy (23 000 cm^{-1}).

The colour of the low-temperature phases of both modifications is bluish white. It becomes instantaneously pale green at the transition point and then changes continuously to brownish yellow at higher temperatures. Because the changes in colour can be directly correlated with the results of the conductivity experiments, it must be concluded that the colour is caused by the electronic band structure and not by an impurity.

(4) *Piezoelectric effect*

Because of its low electrical conductivity it was possible to study the polar properties of the low-temperature phase of WO_3. Thereby it was possible to get some additional information, which is dependent not only on electronic parameters, such as ionic charges, but also on the elastic properties. In other words, the piezoelectric behaviour of a substance near the transition point gives a clue about the possible elastic anomalies during the transformation.

The measurements were made with the reciprocal piezoelectric effect. About 10 mg of powdered crystals were spread uniformly between two Pt plates in a cryostat. An AC voltage of variable frequency was then applied to the plates. The sound waves produced by the consequent variations in the distances between the plates were measured with a microphone and lock-in amplifier. Fig. 6 shows that the transition takes place instantaneously even in the elastic region. The nature of the transformation does not follow the Curie–Weiss law and hence cannot be considered to be due to a cooperative effect of long-range polar interactions, similar to a ferroelectric transformation. It must be primarily attributed to a spontaneous change in the band structure.

(5) *X-ray study*

The cell dimensions of WO_3 were determined from -100 to 900 °C by powder photography. The photographs were made in a specially designed Guinier camera, giving good resolution with minimum background. A further advantage of the camera is that many powder patterns of a substance can be made at different temperatures on the same film. Hence even a slight displacement of the powder lines due to changes in temperature can be observed.

The variations in the cell dimensions of both modifications with temperature are shown in Fig. 7. The lattice constants of the two modifications at room temperature, and those of the orthorhombic (480 °C) and tetragonal (740 °C) modifications are given in Table 1. Fig. 7 shows that the lattice constants change very gradually during the monoclinic–orthorhombic trans-

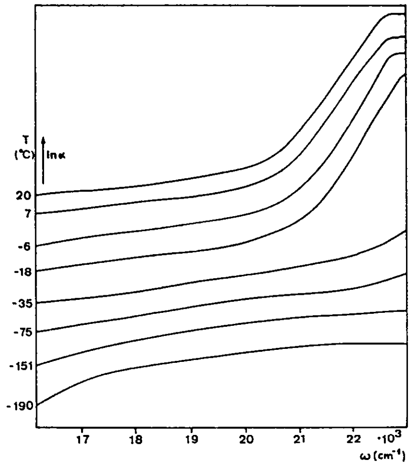

Fig. 4. Absorption spectra of WO_3(II) at low temperatures.

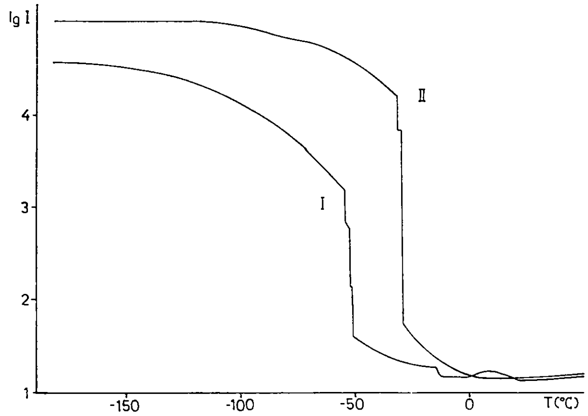

Fig. 5. Temperature dependence of the optical transmission at the frequency $\omega = 23\,000$ cm^{-1}.

formation, whereas they change abruptly during the monoclinic–triclinic and orthorhombic–tetragonal transformations. In particular, the transition to the tetragonal form is characterized by a large decrease in the volume and in *b*.

The monoclinic–orthorhombic transition was also studied with a precession camera and special attention was paid to the superstructure reflections, which reveal the doubling of the *c* axis in the monoclinic variety. Precession photographs of the *hk*0 layer, subjected to very long exposures, show that the additional reflexions are still present in the orthorhombic form, though they are very weak. They further indicate that the extinctions observed in the monoclinic crystal persist in the orthorhombic form; only reflexions *hk*0 with $k=2n+1$, and *h*0*l* with $h+l=2n+1$ are absent. From consideration of all the zellengleichen super-groups, it can be concluded that the space group must be *Pmnb* (D_{2h}^{16}).

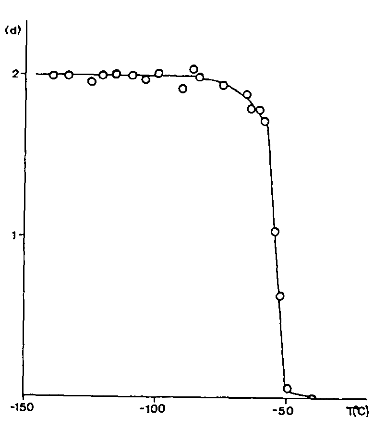

Fig. 6. Variation of the piezoelectric coefficient ⟨*d*⟩ with temperature for WO_3(I).

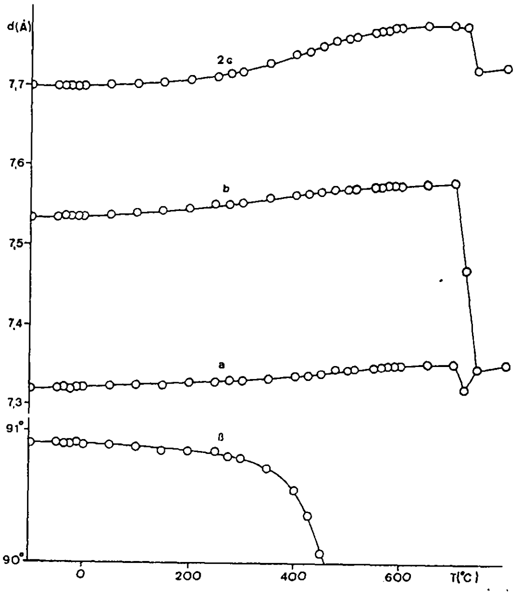

Fig. 7. Lattice constants *versus* temperature for (I).

Discussion

A study of the Raman spectra, electrical conductivity and absorption spectra reveals clearly that the two modifications are similar, but not identical; both show all the (five) discontinuities, but at slightly different temperatures. On the other hand, the X-ray data show that the monoclinic modification undergoes only two transitions, namely, the monoclinic–orthorhombic transition at 480 °C and the orthorhombic–tetragonal transition at 740 °C. The triclinic first becomes monoclinic at about 200 °C with identical lattice constants. Then it behaves just like the monoclinic modification. However, low-temperature photographs (up to −100 °C) of both forms do not show any change. The monoclinic variety is not converted into the triclinic one, as reported by Tanisaki (1960*b*), and Roth & Warring (1966). The conversion of the triclinic variety at −40 °C, as reported by Tanisaki (1960*b*) was also not observed. Hence, it must be assumed that our WO_3 crystals differ from those of the above authors. Nevertheless, lattice constants (Table 1) of the monoclinic and triclinic varieties are the same as those reported by them. To be sure of our result, we placed the monoclinic modification in liquid nitrogen for a few days. A powder pattern of it was made, but no changes were observed. Hence it is difficult to explain this discrepancy.

However, Tanisaki's (1960*b*) measurements of the electrical conductivity of WO_3 agree very well with ours, which, in turn, are compatible with all the other physical properties investigated by us. Both (I) and (II) are piezoelectric insulators at very low temperatures and semiconductors at higher temperatures. This important phase transition alters the physical properties considerably and causes a change in the space group. As we are unable to observe a corresponding change in the powder data, we are convinced that the causes of this phase transition must be found in the finer details of the structure and may not be responsible for the changes in the lattice dimensions observed by Tanisaki at −40 °C. For the same reasons we doubt whether the discontinuity at 17 °C can really be correlated with changes in lattice parameters.

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