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Domain Structure of Tungsten Trioxide

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IT has been found recently that tungsten trioxide, WO_3 , behaves like a ferroelectric.¹ The dielectric constants of sintered ceramics or monocrystals are high compared with those of ordinary solid materials, being 100 to 300 at low temperature and of the order of 10^3 at room temperature. Though the tartrate, dihydrogenphosphate, and barium titanate are found to be analogous to a ferromagnetic, for example, to obey the Curie-Weiss law and to show the multiple domain structure, it is not certain whether WO_3 corresponds to this case.

The present authors obtained single crystals of WO_3 from the melt and were able to observe the details of the multiple domain structure which exhibits phenomena similar to those of BaTiO_3 .² Optical and x-ray observation showed that the crystal has a pseudo-orthorhombic symmetry; $a = 7.278\text{Å}$, $b = 7.460\text{Å}$, $c = 3.838\text{Å}$, and $\beta \sim 90^\circ$ which coincide with the values reported earlier.³ The flat plate of monocrystal obtained was usually smaller than $1 \times 1 \times 0.1 \text{ mm}^3$ in dimensions, with the orthorhombic c -axis parallel to the shortest edge. In many cases each crystal is composed of multiple domains divided by parallel stripes which are oriented at an angle 45° to the plate edges, or sometimes parallel to them.

In some cases, however, the crystal appears almost transparent with faint lines. These domain patterns, which are very like the twinned structure of BaTiO_3 , are shown in Fig. 1a.

A microscopic inspection reveals that the neighboring twin components show pleochroism when observed by rotating the microscopic stage. When the direction of vibration of the polarized light coincides with one of the plate edges of the monocrystal, the contrast between light and dark fields is largest. This indicates the orthogonality of X' -directions for the neighboring twins.

Between crossed Nicols, an extinction effect is observed at positions at which one of the plate edges coincides with the directions of vibration of the polarized light. That is, the a - (or b -) axis in one domain component is perpendicular to the a - (or b -) axis in the neighboring components. In addition, there exist many fine striations parallel to the plate edges, which are nearly orthogonal with each other for neighboring twins (Fig. 1a). The angle between them is about $88^\circ 30'$ and is equal to that between planes (110) and $(\bar{1}\bar{1}0)$, numerically equal to $2 \tan(b/a) = 88^\circ 36'$. Therefore, twinning occurs about $\{110\}$ planes. These fine striations are considered to

be a kind of the crystal habit which specify the a - or b -axis in the orthorhombic lattice.

Wedge-shaped domains like those of BaTiO_3 are also observed (Fig. 1b). In addition there exists fork- or scissors-shaped domains which are variable in shape, corresponding to the stress existing in the crystal. The breadth of the parallel components is about 0.01 to 0.004 mm, which is comparable to those of BaTiO_3 .

When an unidirectional pressure is applied along one of the plate edges, some twins grow in volume by a migration of the twin boundary and wedge-shaped domains disappear gradually. At a fairly large pressure, irreversible boundary migration occurs, giving a crystal without domains. Temperature and electric field seemed to have no distinct effect upon the domain pattern.

X-ray studies of the powder samples and single crystals indicate that there exists no remarkable change in reflections above room temperature, except slight change in intensity above 120°C in the region of high Bragg angle.

It seems that there is no phase change like that of BaTiO_3 for which a transition occurs from a low symmetry type to a high symmetry one at the Curie temperature.

The details of the investigation will be reported elsewhere.

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Nuclear Magnetic Moment of S^{33}

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SEVERAL attempts have been made¹⁻⁴ to determine the nuclear magnetic moment of S^{33} by the Zeeman effect on the microwave rotational spectra of OCS^{33} . Jen^{1,2} first set for $\mu(\text{S}^{33})$ a broad range between 0.6 and 0.9 n.m., but there has not been good agreement on a more exact value. The difficulties encountered appeared to lie principally in the low intensities of the hyperfine lines at the low natural abundance of S^{33} and the uncertainty of the sign of the OCS rotational g -factor.

Recently, a sample of sulfur containing an isotopic abundance of 5.54 percent of S^{33} (7.5 times natural abundance), loaned by the Isotopes Division of the AEC, has made possible a re-examination of the problem under much more favorable conditions. The present paper is the result of a joint effort by the authors to reach essential agreement for the final result on $\mu(\text{S}^{33})$ as measured independently with different experimental methods. Eshbach and Hillger⁴ used a short section of wave guide employing Stark modulation and applied a magnetic field to the whole length of the wave guide. Jen⁵ used a resonant cavity, which is placed between the pole pieces of an electromagnet. In spite of difference in their techniques, the authors have obtained substantially the same result for $\mu(\text{S}^{33})$.

The hyperfine structure of the $\text{OCS}^{33} J=1 \rightarrow 2$ rotational transition was first studied by Townes and Geschwind,⁶ who measured the nuclear quadrupole coupling and determined the nuclear spin, $I(\text{S}^{33})$, as $3/2$. The spin assignment has been confirmed by the present studies. The Zeeman splitting for each of the hyperfine lines has been examined in detail for both the π - and σ -transitions.

The strongest line in the spectrum at zero field represents the joint contribution of two coincident transitions: $F=3/2 \rightarrow 5/2$, and $F=5/2 \rightarrow 7/2$. The Zeeman components of this line are too numerous to be clearly resolved. The variation of intensity of this line as a function of the magnetic field was used in some preliminary experiments^{2,4} for the determination of $\mu(\text{S}^{33})$. The results obtained in this manner are now superseded by much more accurate results derived from the well-resolved splittings of the hyperfine lines.

The Zeeman splittings of the following hyperfine lines have been examined: $F=1/2 \rightarrow 3/2$, $5/2 \rightarrow 5/2$, $1/2 \rightarrow 1/2$, $3/2 \rightarrow 3/2$, and

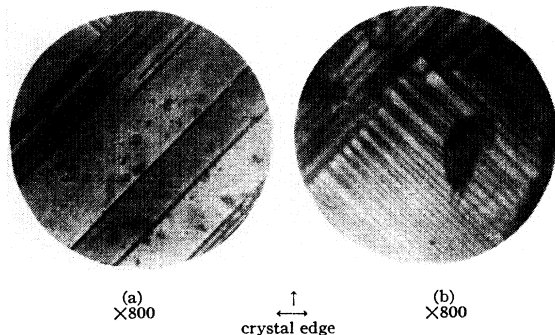


FIG. 1. Multiple domain structure of WO_3 . (a) Domains divided by parallel stripes. (b) Wedge-shaped domains.

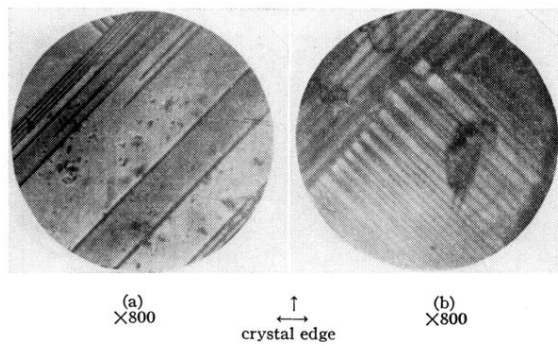


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