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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; $a = 7.278\text{\AA}$, $b = 7.460\text{\AA}$, $c = 3.838\text{\AA}$, 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

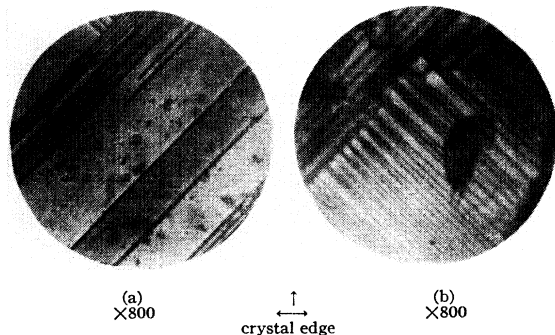


FIG. 1. Multiple domain structure of WO_3 . (a) Domains divided by parallel strips. (b) Wedge-shaped domains.

3/2→1/2. In each instance, there were at least two strong and well-resolved components. The frequency differences between these components have been measured with good accuracy.

It has been found that the observed Zeeman spectra of the OCS³³ $J=1\rightarrow 2$ hyperfine structure are completely consistent with theory^{6,7} if $|g_N|=0.421$, $|g_{mole}|=0.026$, and g_{mole} and g_N have opposite signs. Here, g_N is the S³³ nuclear g -factor and g_{mole} is the rotational g -factor for OCS. The quantity g_{mole} determined here is consistent with the value of g_{mole} determined directly from the OCS³² Zeeman spectrum.

In an attempt to establish the absolute signs of the g -factors, Eshbach⁸ has used an arrangement providing a circularly polarized wave and succeeded in proving that the absolute signs of g_N and g_{mole} are respectively positive and negative.

Using $g(N_{33})=0.421$ and $I=3/2$, the final result for the nuclear magnetic moment of S³³ is

$$\mu(S^{33})=0.632\pm 0.010 \text{ n.m.}$$

This result is within the Schmidt limits and is in agreement with the prediction of the single particle model of nuclear shell structure.

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⁸ A complete report of this work will be published later.

Angular Dependence of Hyperfine Structure for the Copper Ion

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SHORTLY after the discovery of hyperfine structure in solids by Penrose, it was found by a number of independent workers¹ that the experimental results are not in agreement with the theoretical deductions, if one assumes that the electron-orbit-nuclear spin and electron-spin-nuclear spin terms are responsible for the hyperfine separation. A careful experimental investigation by Ingram² has accentuated the discrepancy between theory and experiment. Recently Abragam³ has proposed a theory to account for the experimental results. We would like to suggest in this note another term which is perhaps partly responsible for the angular dependence of hyperfine structure.

A new interaction term was suggested to us by the recent work of England and Schneider⁴ who investigated the absorption properties of the Mn²⁺ ion as activators in zinc sulfide phosphors. The spectroscopic ground state of the ion is ⁶S_{5/2}, and therefore the interaction terms used for the Cu²⁺ ion will give no contribution to the separation. To account for the observed hyperfine splitting it is necessary to use a term⁵ of the form $a_2\mathbf{S}\cdot\mathbf{I}$. Since the d electrons are responsible for the spin in both copper and manganese, we have investigated the consequences of assuming that a_2 is approximately the same for copper and manganese. We have used the interaction potential

$$H' = -a_1\mathbf{L}\cdot\mathbf{I} + a_1\left\{\frac{3(\mathbf{S}\cdot\mathbf{r})(\mathbf{I}\cdot\mathbf{r})}{r^2} - \mathbf{I}\cdot\mathbf{S}\right\} - a_2\mathbf{S}\cdot\mathbf{I} + \gamma\mathbf{H}\cdot\mathbf{I}.$$

This expression differs from that taken by others in that the signs of the first two terms are different, and that the additional $\mathbf{S}\cdot\mathbf{I}$ term is introduced.

It follows from fairly general group-theoretical considerations that for a doubly degenerate electron ground state the above

interaction potential leads to the following term values:

$$E^+ = (g_{11}^2 \cos^2\theta + g_{12}^2 \sin^2\theta) \frac{1}{2} \mu_B H \\ + \left[\left(\frac{\Delta\nu_{11}g_{11}}{2g} + \gamma H \right)^2 \cos^2\theta + \left(\frac{\Delta\nu_{12}g_{12}}{2g} + \gamma H \right)^2 \sin^2\theta \right]^{1/2} m_I, \\ E^- = -(g_{11}^2 \cos^2\theta + g_{12}^2 \sin^2\theta) \frac{1}{2} \mu_B H \\ - \left[\left(\frac{\Delta\nu_{11}g_{11}}{2g} - \gamma H \right)^2 \cos^2\theta + \left(\frac{\Delta\nu_{12}g_{12}}{2g} - \gamma H \right)^2 \sin^2\theta \right]^{1/2} m_I.$$

The symbols $\Delta\nu_{11}$ and $\Delta\nu_{12}$ represent the hyperfine structure component separations in a parallel and perpendicular magnetic field. For the particular case of Cu²⁺ these quantities are given by

$$\Delta\nu_{11} = 2a_1[-4p + (2/7) - 3q/7] + a_2, \\ \Delta\nu_{12} = 2a_1[-q - (1/7) + 3q/14] + a_2/2,$$

where the p and q are certain coefficients appearing in Polder's⁶ wave functions and are related to the g values by $g_{11}=2(1-4p)$ and $g_{12}=2(1-q)$.

The results of the above equation can be used to determine the relative values of a_1 and a_2 . For the g values we take $g_{11}=2.44$ and $g_{12}=2.06$. Ingram gives $\Delta\nu_{11}/\Delta\nu_{12}=g_{11}\Delta H_{11}/g_{12}\Delta H_{12}=8.3$. These numerical values lead to $a_1=0.88a_2$. The average separation of adjacent lines in manganese is 68 gauss which corresponds to an energy separation of $2\mu_B\Delta H=1.25\times 10^{-18}$ erg. For a copper ion in a parallel field $\Delta\nu_{11}=g_{11}\mu_B\Delta H=a_1+a_2$. Assuming that a_2 is the same for both copper and manganese we obtain $\Delta H=118$ gauss, which gives an over-all separation of 354 gauss. This value is in good agreement with Ingram's value of 350 gauss.

After completing this investigation we have heard indirectly that J. M. Jauch has come to similar conclusions.

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Spin-Spin Interaction within Paramagnetic Ions

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THAT the magnetic spin-spin interaction (W_{SS} , say) between pairs of electrons in an atom can cause deviations from the Landé interval rule is well known in spectroscopy. The effect is usually relatively small, although in helium it completely distorts the triplet terms. The purpose of this letter is to point out its possible role in the microwave resonance behavior of certain paramagnetic salts. The cases of interest occur where the splitting of the lowest spin multiplet of the paramagnetic ion, due to the combined action of the crystalline potential V and the spin-orbit interaction W_{LS} , either vanishes to second order in W_{LS} , or is very small. The splitting may then be dominated by W_{SS} .

In the salts of the iron transition group the ions Mn²⁺ and Fe³⁺, which are in a $3d^5$ ⁶S state, furnish examples of interest. Their splitting has been studied by Van Vleck and Penney,¹ who consider various higher order processes involving V and W_{LS} through intermediate excited electronic states, using order of magnitude arguments to estimate the resulting splitting: but detailed calculation shows that their estimates are too high and that the mechanisms they propose are inadequate to explain the observed splittings. The important mechanisms would actually appear to be (a) a second-order process involving the first powers of W_{SS} and $V_2=H'(2z^2-x^2-y^2)$ via the intermediate state $3d^4s$ ⁶D, giving a contribution DS_2^2 to the sub-Hamiltonian, and (b) a fifth-order process, quartic in W_{LS} and linear in $V_4=-G'(x^4+y^4+z^4+3y^2z^2-3z^2x^2-3x^2y^2)$, through intermediate states formed from $3d^5$, giving a contribution $(a/6)(S_x^4+S_y^4+S_z^4)$. Experimental evidence indicates that (a) dominates in manganese salts,² and (b) in ferric salts.³ This changeover is not surprising, for (b) increases with a very high power of the effective nuclear charge of the ion.