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Electron spin resonance of defects in single crystal and thin films of tungsten trioxide

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The ESR spectra of single crystals and amorphous thin films of WO_3 have been measured in the temperature range 77–300°K. In the case of single crystal the observed resonance lines were identified as due to Mo^{5+} ions. The observed values are: $g_I = 1.776$, $g_{II} = 1.796$, and $g_{III} = 1.833$ and the hyperfine splitting constants are $A_I = 0.0029$, $A_{II} = 0.0026$, and $A_{III} = 0.0074$. In the case of thin-film broad resonance absorption at $g = 2.012$ and $g = 1.918$ was observed for colorless film which on electrocoloration showed an additional resonance at $g = 1.75$. The temperature dependence of the electrical conductivity and spin density gave activation energies of 0.21 and 0.04 eV, respectively.

INTRODUCTION

The transition-metal oxides such as WO_3 are large-band-gap (~3.5-eV) insulators with the valence band consisting primarily of oxygen $2p$ states and the conduction band arising from the tungsten $5d$ states. Since the W^{6+} ion in WO_3 has a $5d^0$ configuration, the conduction band is ordinarily empty and, therefore, the material is expected to be an insulator. From the optical and electrical properties of a thin film of WO_3, the band gap has been found to be around 3.5 eV at room temperature.[1]

Single crystals of WO_3, grown by the vapor-transport technique, show an optical absorption edge at considerably longer wavelengths (~2.7 eV) giving rise to a dark-green color of the crystal. The conductivity of the crystal is a factor of 10^7 higher than that of the amorphous WO_3 film and many orders of magnitude higher than that to be expected for intrinsic free carriers. On crystallization of the film the conductivity increases by two orders of magnitude but is still considerably less than that of the single crystal. Berak and Sienko[2] have extensively studied the transport properties of single crystals of WO_3 as a function of deviation from stoichiometry. Apparently, the presence of shallow donor states associated with defects such as oxygen vacancies, dislocation rings or W-W interaction pairs is responsible for the free carriers.

It appears likely that the presence of oxygen vacancies may be at least partially associated with the reduction of W^{6+} to W^{5+} which should be detectable by ESR measurements since the W^{5+} ion has an unpaired d electron. Moreover, thin films of WO_3 made by standard evaporation techniques form large densities of color centers when excited by an ionizing radiation or under an applied electric field. The formation of color centers is also associated with an increase in electrical conductivity by several orders of magnitude which in some cases makes it metallic. It seems equally probable that the coloration and the increase in conductivity may be associated with defect states in this material.

To our knowledge no measurements of the ESR spectra of single crystals or thin films of WO_3 have been reported. In an effort to understand the origin of the conduction electrons and color we have studied the ESR spectra of a single crystal and an electrically colored thin film of WO_3. The results suggest that the ESR signal is due to the presence of the Mo^{5+} ($4d^1$) ion instead of the expected W^{5+} ion. The color centers in the thin film of WO_3 give an entirely different ESR spectrum which may be attributed to a W^{5+} ion or a complex defect involving W^{5+} ions and oxygen vacancies.

EXPERIMENTAL RESULTS

The ESR spectrum was measured with a Thomson-CSF Model THN-251 X-band spectrometer in the frequency range 900–9500 MHz and in the temperature range of 77–298 °K. The signal was observed visually on an oscilloscope and the derivative of the absorption curve was recorded on an x-y recorder.

The single crystals of WO_3 used in this experiment were obtained from Walkyns, Clarendon Laboratory, Oxford who grew these crystals by the sublimation technique. The rectangular platelets of these crystals were dark green in color and had an average size of approximately 4 × 2 × 0.5 mm. X-ray diffraction studies on the crystal show that there exists some twinning in the crystal and the twinning angle was roughly 3°. The c axis of the crystal was perpendicular to the ab plane of the crystal platelet. The crystal was mounted in the liquid-nitrogen cryostat with the c axis either parallel or perpendicular to the mag-

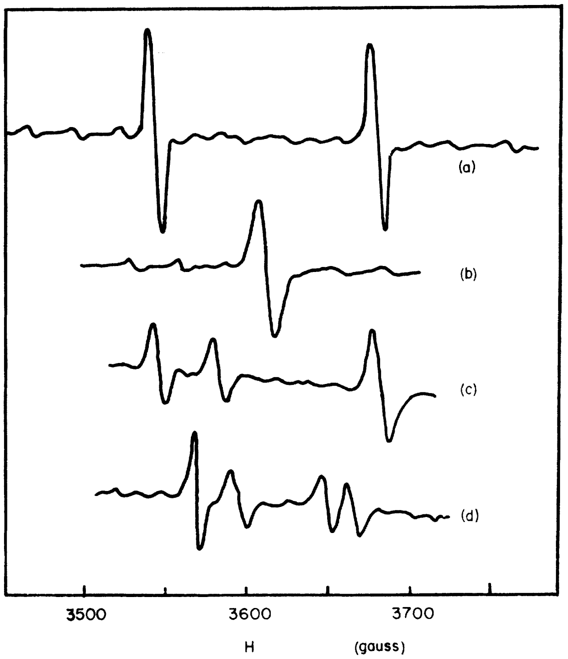

FIG. 1. Typical derivative curve of the resonance lines of WO_3 single crystal measured at 77 °K as a function of orientation: (a) 0°, (b) 45°, (c) 25°, (d) 20°.

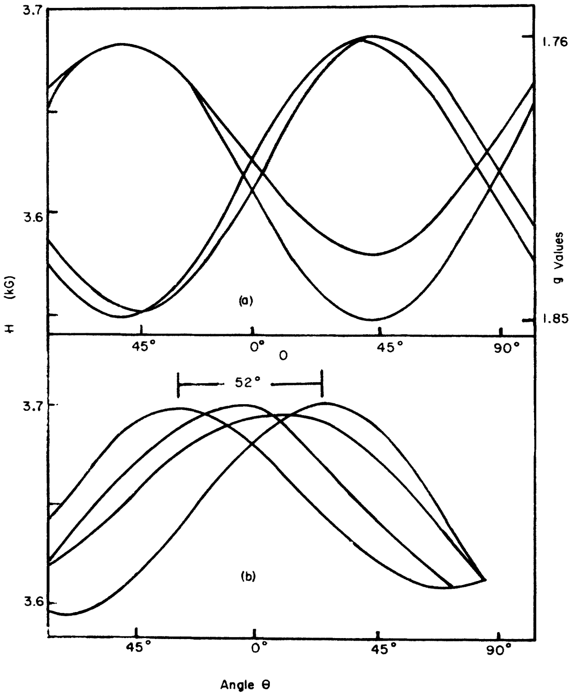

FIG. 2. Angular dependence of the line position on rotating along the *ab* plane: (a) and (b) are two different crystals randomly selected from the same batch.

netic field. A typical trace of the derivative curve of the resonance lines at 77 °K is shown in Fig. 1. The linewidth of the principal absorption is around 7 G. When the external magnetic field is directed along a crystallographic axis, parallel to either the *a* or the *b* axis, the two sets of lines have the widest separation from each other. When the external magnetic field is at 45° to either of these directions the two sets of lines coincide. At intermediate angular directions, each of these two principal lines split into two lines. The angular dependence of the line position for two different crystals are shown in Figs. 2(a) and 2(b). It is important to note that it is difficult to get single crystals of WO_3 free from twinning and some of the complexity in the angular dependence comes from that.

Each of these two principal lines have six satellite hyperfine lines. The number of the hyperfine lines and their nearly equal spacing indicate that the resonance is due to the hyperfine structure of isotopes with the nuclear spin $I=\frac{5}{2}$. The most likely candidate would be Mo ions. The odd isotopes of Mo ions are ^{95}Mo and ^{97}Mo which have a natural abundance of 15.7% and 9.6%, respectively, and their nuclear magnetic moments are −0.9099 and −0.9290 nuclear magneton, respectively. The intensity ratio of the principal line and the hyperfine lines corresponds to the relative isotope abundance of the odd and even Mo^{5+} ions. The center line could, therefore, be identified with the resonance absorption of Mo ions with zero nuclear spin, and the hyperfine lines are due to the nonzero nuclear spin of the Mo ions. Each hyperfine line is expected to split into two lines because of their differences in the nuclear spin but it could not be resolved. The concentration of Mo ions in the crystals was not available to correlate with the spin density.

While no resonance absorption was observed at room temperature an intense absorption was detected at 77 °K. On increasing the temperature from 77 °K toward room temperature the absorption broadened considerably and then disappeared abruptly at 262.5 °K. The phase transition at this temperature is associated with an increase in conductivity of the crystal by a factor 10^4 as shown in Fig. 3. A single crystal of WO_3 with indium contacts shows a first-order phase transition at 277 °K during the cooling cycle and at 245 °K during the warming cycle. At the transition point the resistivity changes by several orders of magnitude. Similar transition in WO_3 single crystals has been observed previously.[3,4] The disappearance of the ESR signal at this point could be due to the increased density of free carriers. The small discrepancy in the transition point could be within

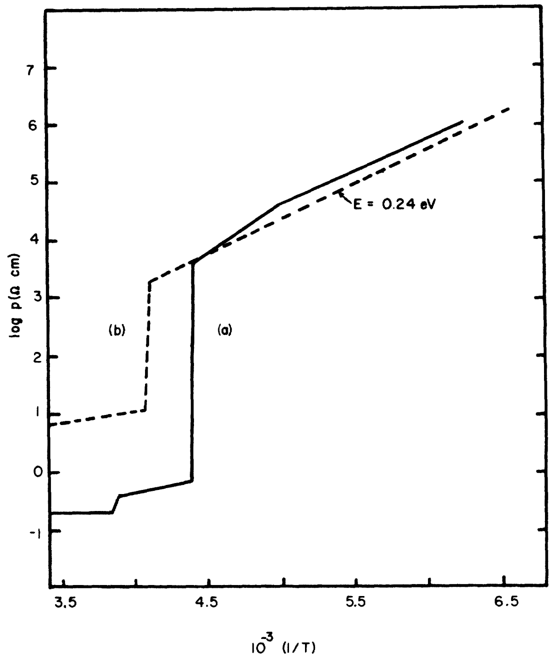

FIG. 3. Logarithms of the resistivity of a WO_3 crystal as a function of reciprocal temperature: (a) during cooling, (b) during heating.

the limit of experimental error in reading the true temperature of the crystal in the resonance cavity.

The ESR line shape at 77 °K was found to be nearly Gaussian. With increasing temperature the lines broaden but the position of the absorption maximum remains unchanged. The half-width (ΔH) was determined as the distance between the maximum and minimum points of the derivative curve. Assuming that the product of ΔH and the intensity of absorption is directly proportional to the number of spins, the plot of $\ln(I\Delta H)$ against $1/T$ gives a straight line as shown in Fig. 4. From this curve the temperature dependence of the half-width is given by the relation $I\Delta H \propto e^{-\Delta E/RT}$, where $\Delta E = 0.041$ eV or 330 cm^{-1}. The position of the absorption lines can be described by a spin Hamiltonian of the form

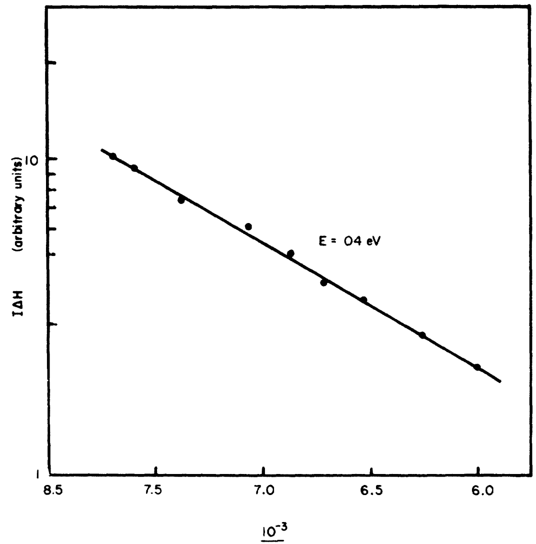

FIG. 4. Logarithms of electron spin density ($I\Delta H$) plotted as a function reciprocal temperature.

$$H = (g_x S_x H_x + g_y S_y H_y + g_z S_z H_z) + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z ,$$

TABLE I. g factors and the hyperfine coupling constants of Mo^{5+} ion in different host matrices.

Material Mo^{5+} ion in:	g factor	Hyperfine coupling constants (cm^{-1})	Temp. (°K)	Ref.
$K_3(InCl_6)\,2H2O{:}Mo^{5+}$	$g_{\mathrm{I}} = 1.929$ $g_{\mathrm{II}} = 1.951$	$A_{\mathrm{I}} = 0.0039$ $A_{\mathrm{II}} = 0.0079$	20	5
K_2SnCl_6	$g_{\mathrm{I}} = 1.939$ $g_{\mathrm{II}} = 1.974$	$A_{\mathrm{I}} = 0.0035$ $A_{\mathrm{II}} = 0.0077$	•••	6
$CaWO_4$	$g_{\mathrm{I}} = 1.887$ $g_{\mathrm{II}} = 1.987$	$A_{\mathrm{I}} = 0.0041$ $A_{\mathrm{II}} = 0.0008$	4.2	7
TiO_2	$g_{\mathrm{I}} = 1.788$ $g_{\mathrm{II}} = 1.812$ $g_{\mathrm{III}} = 1.913$	$A_{\mathrm{I}} = 0.0031$ $A_{\mathrm{II}} = 0.0025$ $A_{\mathrm{III}} = 0.0066$	77	8
MoO_3	$g_x = 1.942$ $g_y = 1.953$ $g_z = 1.878$	$A_x = 0.0032$ $A_y = 0.0029$ $A_z = 0.0069$	•••	9
WO_3	$g_{\mathrm{I}} = 1.776$ $g_{\mathrm{II}} = 1.796$ $g_{\mathrm{III}} = 1.833$	$A_{\mathrm{I}} = 0.0029$ $A_{\mathrm{II}} = 0.0026$ $A_{\mathrm{III}} = 0.0074$	77	This work

where effective electron spin is $S=\frac{1}{2}$ and nuclear spin is $I=\frac{5}{2}$. The hyperfine coupling constants were calculated from the absorption line position and at a temperature of 77 °K. The resulting values of the constants along with similar measurements of Mo^{5+} in other host lattices are given in Table I.

THIN FILMS OF WO_3

Thin films of WO_3 (1 μm thick) were evaporated on NESA glass and were colored electrolytically to form an intense-blue color. The ESR spectra of the film material after scraping from the NESA glass surface was then measured at 77 °K both before and after coloration. The uncolored film gives two resonance absorption at $g=2.012$ (weak) and $g=1.918$ (moderate). On electrocoloration the intensity of signals at $g=2.012$ decreases slightly, $g=1.918$ increases somewhat, and a new signal at $g=1.75$ (moderate) appears. On warming to room temperature the $g=1.918$ and 2.012 signals remain unchanged but the $g=1.75$ signal broadens considerably and becomes much weaker. On heating the colored film to 400 °C for 4 h the color centers disappear completely with simultaneous disappearance of all the ESR signals.

DISCUSSION

It is apparent from Table I that the measured g values and the hyperfine structure observed in WO_3 is typical of the Mo^{5+} ion. The presence of Mo^{5+} ion in the WO_3 crystals suggest that these crystals are presumably nonstoichiometric and contain oxygen ion vacancies which charge compensate for the Mo^{5+} ions. The crystals were prepared by the vapor-phase growth technique in air and during the growth process some oxygen was lost and the vacancies were stabilized by the Mo^{5+} ions. There was no evidence of W^{5+} ions in the ESR spectra which with $S=\frac{1}{2}$ and $I=\frac{1}{2}$ should show a hyperfine doublet. The preferential reduction of the Mo ions in WO_3 crystals is probably due to the lower binding energy of oxygen ions to Mo^{6+} ions as compared to the W^{6+} ions. Similar preferential reduction of Mo^{6+} ions has been observed previously in $CaWO_4$ host lattices.[7]

The angular dependence of the ESR spectra as shown in Figs. 2(a) and 2(b) are quite complex but the line position shows a definite periodicity which confirms that Mo^{5+} ions go into the host lattice substitutionally. The two sets of lines which converge into one line after approximately 90° rotation could be due to the difference in the local site symmetry of the Mo^{5+} ions. The macroscopic structure of the WO_3 lattice at low temperature (below 233 °K) is triclinic and the local symmetry of the W^{6+} ion although not known at low temperature could be similar to that observed with the room-temperature modification. At room temperature the crystal is monoclinic and is composed of two nonequivalent WO_6 octahedra in which the W-O bond distances differ considerably.[10] These octahedra are arranged in such a way that a shorter distance and a longer one are linked alternately as shown in Fig. 5 where $W_{(1)}$ and $W_{(2)}$ represent two nonequivalent positions. Therefore, the substituted Mo^{5+} ions will have two different local site symmetries available. The angular dependence of the ESR spectra suggest that the low-temperature modification (triclinic) is formed by only a slight distortion of the monoclinic structure and this is further substantiated by the crystal structure determination which shows that the lattice parameters change only slightly on phase transition.[3]

Another interesting feature of the WO_3 crystal is the presence of a green band that appears under polarized light in oxygen deficient WO_3. The bands invariably form an angle of 52°–54° with each other when viewed in the a-b plane. They were tentatively identified by Sienko and Berak[3] as regions where the octahedra have collapsed to form Magneli shear planes. It is interesting to note that in some crystals, which show these bands, the maximum in the angular variation of the Mo^{5+} lines as shown in Fig. 2(b) shows a separation of 52°.

The splitting of each of the main lines into a doublet at small deviation from the main crystallographic axes as shown in Fig. 1 is not understood but it could be either due to twinning or due to the presence of protons in the vicinity of the Mo^{5+} ions as observed in the case of Mo^{5+} ions in MoO_3 single crystals.[11]

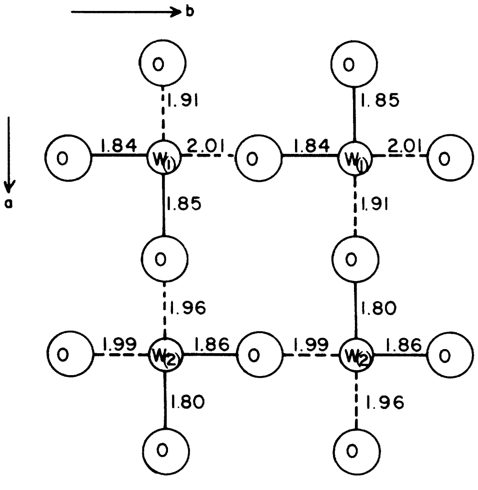

FIG. 5. W-O bond distances given in Å along a and b direction showing two nonequivalent tungsten atoms.

The temperature dependence of the Mo^{5+} electron spin density as shown in Fig. 4, gives an activation energy of 0.04 eV which does not agree with the activation energy of 0.24 eV obtained on the same batch of crystals from the electrical-conductivity measurement in the same temperature range as shown in Fig. 3. However, Berak and Sienko[2] have observed an activation energy in the range 0.03–0.05 eV in the electrical-conductivity measurement on WO_3 single crystals which they attribute to the presence of oxygen vacancies or W-W interaction pair that results from the collapse of a shared octahedron corner which forms a donor state. The activation energy of 0.04 eV observed in this case could also be interpreted as due to an Orbach-type relaxation process in which the absorption of a phonon excites the spin system to a higher level followed by emission of another phonon of different energy so that a magnetic ion is indirectly transferred from one level to the other of the ground-state doublet.

In the absence of any hyperfine structure it is not possible to make any analysis of the ESR spectra of thin films of amorphous WO_3. The most-significant result is the appearance of a signal at $g=1.76$ in the electrically colored WO_3 film which can be tentatively identified as due to W^{5+} ions. Although g values of W^{5+} ions in crystalline matrices[12] are considerably less (1.45, 1.47, 1.59 in TiO_2) than the observed value, in glassy matrices g values in the range 1.65–1.76 have been observed.[13] The appearance of two signals at $g=2.012$ and $g=1.918$ in the uncolored state which remains essentially unaffected by coloration is difficult to interpret. It is probable that the weak signal at $g=1.918$ is due to transition metal ion impurities such as Mo^{5+} ion. However, an accurate analysis of the impurity contents of the film is required before any definitive statement can be made.

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