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Electrical transport and EPR properties of the α, β, and γ phases of Fe_2WO_6

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The polymorphic modifications α, β, and γ Fe_2WO_6 of the iron (III) tungstate have been investigated by resistivity and electron paramagnetic resonance (EPR) measurements. The high-electrical resistivity for all phases complies with the dominant antiferromagnetic component of the compounds. The EPR spectra comprise a broad exchange narrowed EPR line due to Fe^{3+} ions. The broadening of the EPR linewidth is explained in terms of the critical spin fluctuations near the antiferromagnetic phase transition. The shift of the resonance field and the temperature dependence of the EPR intensity imply an extended region of short-range order correlations. [S0163-1829(99)09535-1]

Iron-tungsten-oxygen system, especially the Fe_2WO_6 phase continues to attract much attention from both fundamental and applied perspective. These materials have been the subject of many experimental studies aimed to establish the correlation among their structural, magnetic, and conducting properties.[1–10] They are also promising for device fabrication, more specifically in systems for the direct conversion of solar to electrical energy.[10] Crystallographic studies have revealed the existence of three structural modifications of Fe_2WO_6.[1–5,8] The low-temperature modification (α-Fe_2WO_6) when the synthesis is carried out below 800 °C, the high-temperature modification (γ-Fe_2WO_6) prepared at temperatures above 900 °C and the recently discovered polymorphic modification (β-Fe_2WO_6) obtained in the temperature range of 750–840 °C.[8] The α and γ phases crystallize in the columbite and tri-α-PbO_2 structures respectively, both preserving the orthorhombic symmetry (*Pbcn*), while the β phase in the monoclinic one.[8]

Neutron diffraction measurements from room temperature (RT) down to 4.2 K, have confirmed the crystal structure of the γ phase, which has been found to be antiferromagnetic with $T_N \sim 240\,\mathrm{K}$.[3,4] An increase in intensity of several reflections allowed by *Pbcn* has been also detected starting from $T \sim 150\,\mathrm{K}$, associated with a shift of ionic positions.[4] The magnetic susceptibility of the γ phase follows Curie-Weiss behavior above 600 K with effective magnetic moment close to that of Fe^{3+} ($S=\frac{5}{2}$), while a nonlinear behavior indicative of short-range magnetic correlations was observed in the range of 300–600 K.[5] However, measurements below 300 K for the α and γ phases have shown that apart from a peak at 250 K, which is consistent with the antiferromagnetic ordering, a significant paramagneticlike contribution grows at lower temperatures with a maximum at 15 K.[9] Another peak whose origin is not clear, has been detected at ~200 K, while for the β phase a more complex behavior has been observed, comprising a discontinuity of the magnetic susceptibility at 150 K.[9] Low-temperature (4–20 K) electron paramagnetic resonance (EPR) measurements have revealed the presence of isolated iron centers,[9] while measurements at $T = 40-250\,\mathrm{K}$ for the α phase revealed the presence of a broad Fe^{3+} EPR line with divergent variation when approaching 200 K.[11] In this context, a comparative study of the magnetic and electrical properties of the polymorphic modifications α, β, and γ-Fe_2WO_6 of the iron-tungsten system has been undertaken using resistivity and EPR measurements.

The preparation procedure for the three α, β, and γ polymorphic modifications of Fe_2WO_6 has been described in previous work.[8] The polycrystalline samples have been identified by x-ray diffraction as single phase using a Dron-3 x-ray diffractometer utilizing Co $K\alpha$-radiation. The lattice constants are similar to those reported earlier.[8] EPR measurements were carried out on fine powder samples with a standard x-band spectrometer (Radiopan SEX-104) employing a resistance flow cryostat system in the temperature range of 200 to 470 K. dc electrical resistivity measurements were made in the temperature range of 100 to 340 K in small pellets produced under pressure of 70–80 bar. The resistance was measured with a Keithley 181 electrometer according to the two-point geometry, with a higher limit of $2\times10^{11}\,\Omega$ under the circuity of the experiment.

The temperature dependence of the resistivity ρ for the α, β, and γ-Fe_2WO_6 phases is shown in Fig. 1. For all samples, $\rho(T)$ strongly increases by four orders of magnitude with decreasing temperature within the studied temperature range, while a negative temperature coefficient is also observed, both results indicating semiconducting materials. For the β phase $\rho(T)$, which attains the highest value among the three phases, reaches the limiting value of $10^{11}\,\Omega\,\mathrm{cm}$ already at 265 K. Its temperature dependence follows $\rho(T)=\rho_0 e^{E_A/kT}$ with an activation energy $E_A = 0.75\,\mathrm{eV}$ derived from the slope of the linear plot $\ln\rho$ $1/T$ (Fig. 1). The activation energy and room-temperature resistivity of the β phase are comparable to those reported for the *n*-type antiferromagnetic semiconductors $Fe_2V_{4-x}Mo_xO_{13}$ with low-Mo content,

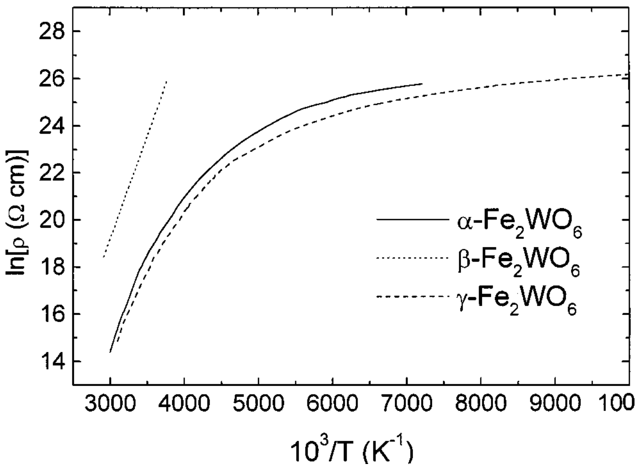

FIG. 1. The electrical resistivity (ln *ρ*) vs 1000/*T* for the *α*, *β*, and *γ* phases of Fe_2WO_6 in the temperature range 100 to 340 K.

where a small amount of Fe^{2+} ions is induced by the substitution of V^{5+} by Mo^{6+} ions in $Fe_2V_4O_{13}$.[12] Such a process has been suggested to occur in iron tungstate as well, by the solid solution of $FeWO_4$ in Fe_2WO_6, thereby introducing Fe^{2+} and Fe^{3+} in equivalent sites in the iron chains.[5]

The room-temperature resistivity for the *α* and *γ* phases is two orders of magnitude lower than that of the *β* phase. The variation of $\rho(T)$ does not follow a simple exponential behavior. As temperature decreases the slope of the ln *ρ* vs 1/*T* graph changes resulting in a gradual change of the activation energy. Considering the highest and lowest temperature range, the corresponding activation energies are obtained (Table I). The relatively low values of E_A comply with the extrinsic type of conductivity of the materials rather than intrinsic conduction. Similar behavior of $\rho(T)$ has been observed in the antiferromagnetic $FeVO_4$ and $FeVMoO_7$, oxides.[12] The latter iron oxides, which are *n*-type semiconductors, exhibit high electrical resistivity as well, while charge transport has been suggested to occur through the thermal-activated hopping of 3*d* electrons via oxygen vacancies.[12] A ^{57}Fe Mossbauer investigation of the *γ* phase, has shown that no significant concentration of Fe^{2+} ions could be detected, while it has confirmed the nonstoichiometric nature of Fe_2WO_6.[7] Accordingly, a similar charge transport as in iron-vanadium oxides may be suggested in the oxygen-deficient Fe_2WO_6 system. The different activation energies may arise from the presence of different donor levels, while the strong temperature dependence of $\rho(T)$ is probably caused by changes of both the concentration and mobility of current carriers that may be strongly thermally activated.[13] The lower crystal symmetry (monoclinic) of the *β* phase compared with the *α* and *γ* phases, might result in a higher degree of cation disorder in the iron-tungsten zig-zag chains,[2] which may correlate with the increase of the resistivity.[14]

TABLE I. Room-temperature resistivity and activation energies for the *α*, *β*, and *γ* phases of Fe_2WO_6.

	ρ	E_A [eV]	
Fe_2WO_6	10^7 [$\Omega\cdot$cm]	$T<160$ K	$T>250$ K
α	3.5	0.04	0.75
β	399	0.75	0.75
γ	1.8	0.05	0.49

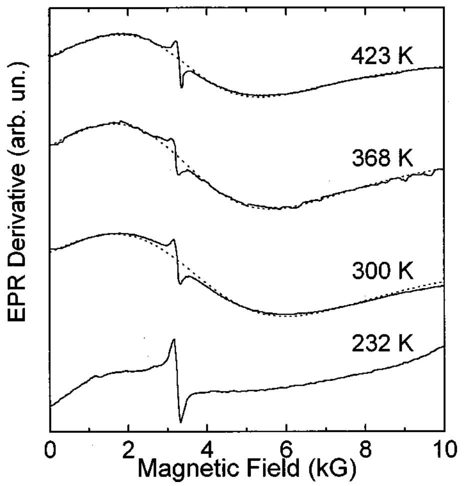

FIG. 2. Temperature dependence of the EPR spectrum for the *β* phase of Fe_2WO_6. The dotted lines correspond to the simulated Lorentzian line shape.

The EPR spectra of the three iron-tungstate phases at RT are dominated by a very broad, slightly asymmetric EPR line with line shape close to the Lorentzian one. The EPR parameters $g_{\mathrm{eff}}=h\nu/\mu_B H_0$ and the half width at half height ΔH at RT, derived by fitting with the appropriate Lorentz line shape,[16] are $g_{\mathrm{eff}}=2.033(5)$, $\Delta H=2250(10)$G, $g_{\mathrm{eff}}=1.85(1)$, $\Delta H=4433(20)$ G, and $g_{\mathrm{eff}}=2.046(5)$, $\Delta H=3370(10)$ G for the *α*, *β*, and *γ* phases, respectively. The obtained g_{eff} values and the strong intensity of the EPR line are in agreement with the *g* value for high-spin Fe^{3+} ions and the bulk iron concentration. The broad linewidth is consistent with the high-iron concentration and the concomitant dipole-dipole and exchange interactions causing exchange narrowing of the dipolar-broadened EPR line.[15] A recent EPR study of Fe^{3+} ions doped in Bi_2WO_6 showed the presence of zero-field splitting much larger than the Zeeman one for Fe^{3+} centers introduced either in the WO_6 octahedra or the Bi_2O_2 layers.[16] This effect for the Fe_2WO_6 oxide, which comprises similar FeO_6 octahedra, may contribute significantly in the second moment of the resonance line and the broadening of ΔH. A narrow EPR line on the center of the broad EPR spectrum in the *β* phase due to isolated Fe^{3+} defects, has been also detected.

Figure 2 shows examples of the EPR spectra for the most recently discovered *β* phase. The temperature dependence of the corresponding EPR parameters, g_{eff} and ΔH, are shown in Figs. 3(a) and 3(b). The EPR linewidth exhibits a rapid increase as temperature decreases, most pronounced at temperatures below 300 K, while at lower temperatures where the antiferromagnetic phase transition is expected to occur, the EPR line is hardly observable due to excessive broadening. The increase of ΔH is usually observed in anisotropic antiferromagnets due to the slowing down of spin fluctuations as the critical temperature is approached from above.[17,18] The latter causes the divergence of the spin-correlation length, which in turn affects the spin-spin relaxation time of exchange narrowed EPR lines resulting in the critical broadening of the EPR linewidth in the vicinity of

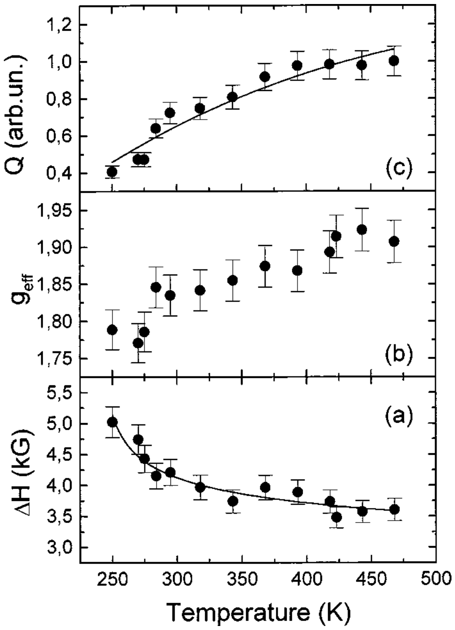

FIG. 3. Temperature dependence of the EPR parameters for the β phase of Fe_2WO_6. (a) linewidth ΔH, (b) g_{eff}, and (c) reduced EPR intensity Q,. The solid lines correspond to the best fit curves derived from Eqs. (1) and (2).

T_N.[17,18] In this case, the temperature variation of ΔH can be described by[18]

$$\Delta H = \Delta H_\infty + A\left(\frac{T-T_N}{T_N}\right)^{-\gamma}, \tag{1}$$

where the first term describes the high-temperature exchange narrowed linewidth, which is temperature independent, while the second reflects the critical behavior with T_N being the Nèel temperature and γ the critical exponent. The best fit procedure to the experimental points resulted in the values $\Delta H_\infty = 2000(100)$ G, $A = 1574(60)$ G, $\gamma = 0.22(2)$, and $T_N = 240(8)$ K. The value of T_N is close to the temperature where the first anomaly in the magnetic susceptibility curve has been observed and where the antiferromagnetic transition is expected.[4,9] On the other hand, the Nèel temperature inferred from $\Delta H(T)$ for the α phase appears lower ($T_N \approx 200$ K) (Ref. 11) and complies with the second anomalous peak in the corresponding magnetic susceptibility.[9] The value of γ is comparable with the values of 0.55 and 0.33 reported for the antiferromagnetic $Fe_2V_{4-x}Mo_xO_{13}$ and $FeVO_4$ iron oxides,[19,20] though much lower than the value of $\frac{5}{3}$ predicted theoretically by Huber for uniaxial antiferromagnets with dipolar anisotropy.[18] According to Kawasaki,[17] the critical exponent can be expressed as $\gamma = -[\frac{1}{2}(7+\eta)\nu - 2(1-\alpha)]$ where ν, η, and α are the critical exponents describing the divergence of correlation length, static correlations, and specific heat, respectively. Using the values of $\eta = \alpha = 0$ and $\nu = \frac{2}{3}$ for the Heisenberg model,[17] γ becomes equal to $\frac{1}{3}$, a value that is closer to the present result. A linear temperature dependence of ΔH for $T \gg T_N$ has been frequently reported in antiferromagnetic systems,[21] that has been suggested to originate from mechanisms as phonon modulation of antisymmetric or/and anisotropic exchange interaction or the temperature dependence of static spin correlations and isotropic exchange.[21,22] Introducing a linear T term in Eq. (1) results in an equally satisfactory fitting of $\Delta H(T)$ and yields a positive coefficient of 1 G/K for the linear term and the values of $\gamma = 0.33(6)$ and $T_N = 221(10)$ K. In this case, the value of the critical exponent approaches more closely the theoretical value of $\frac{1}{3}$ and the values reported for other iron oxides.[19,20] However, due to the weak spin-phonon coupling in the S state Fe^{3+} ions,[23] the linear T dependence, if present at all, might be related to the temperature dependence of exchange that can be induced by the thermal expansion of the lattice.

A pronounced temperature variation is also observed in g_{eff}, which decreases continuously in the whole temperature range [Fig. 3(b)]. The resonance line in antiferromagnets may shift with decreasing temperature due to the effects of short-range order and bulk magnetization.[24–26] Large temperature-dependent g shift has been detected and analyzed theoretically for one-dimensional Heisenberg systems where short-range order dominates over an extended temperature range compared with the three-dimensional case.[24–26] The g shift arises from the anisotropic magnetic susceptibility due dipolar interaction and single-ion anisotropy and is enhanced by short-range order effects.[26] However, no satisfactory theory has been so far reported for higher dimensional systems.[21] In the present case, due to the powder EPR spectrum and the relatively high temperature the magnetization effect should be suppressed supporting the presence of short-range order. Then, the observed g shift from 470 K would imply that short-range order becomes effective at least from temperatures $T \approx 2T_N$.

Analysis of the integral intensity $I(T)$, derived by double integration of the first derivative of the EPR line, shows that $I(T)$ which is proportional to the spin susceptibility, increases with decreasing temperature faster than T_1 implying antiferromagnetic interactions. According to the simplified cluster model for an antiferromagnetic system, where each ion is assumed to belong either to an antiferromagnetic cluster or to well-defined excited state corresponding to the paramagnetic one with constant excitation energy ΔE, the reduced EPR intensity $Q = I(T)\cdot T/I(T_1)\cdot T_1$ ($T_1 = 468$ K) at $T > T_N$ is described by[27]

$$Q \approx \frac{\exp(-\Delta E/kT)[1+(2S+1)\exp(-\Delta E/kT_1)]}{\exp(-\Delta E/kT_1)[1+(2S+1)\exp(-\Delta E/kT)]}. \tag{2}$$

Fitting $Q(T)$ with Eq. (2) for $S = \frac{5}{2}$, results in the value of $\Delta E/k = 738(37)$ K for the energy gap between the bounded antiferromagnetic and excited paramagnetic state [Fig. 3(c)]. The value of ΔE, which is much larger than T_N, also implies that short-range order may be present in an extended temperature region above the Nèel temperature in the β phase.

Comparing the EPR results for the α, β, and γ phases of Fe_2WO_6 we conclude that a dominant antiferromagnetic component due to trivalent iron is present in all cases. In the β phase an extended region of short-range order correlations might be present above the antiferromagnetic transition, while the critical broadening of the EPR linewidth causes the disappearance of the EPR spectrum at higher temperatures (250 K) than in the α phase (210 K) and indicates a rise of the corresponding T_N. Accordingly, a more pronounced antiferromagnetic character can be implied for the β phase relatively to the other phases, which may correlate with the higher electrical resistivity observed for the same compound. In this respect, a correlation between the antiferromagnetic component and the electrical resistivity might be present in the α, β, and γ-Fe_2WO_6 phases of the iron-tungsten system, which warrants further investigations.

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