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Magnetic properties of the phases $Fe_2V_4O_{13}$, $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$

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The Curie constant, C, Weiss constant, θ, effective magnetic moment, μ_{eff}, and spectroscopic splitting factor, g, were determined for the Fe^{3+} ions in $Fe_2V_4O_{13}$, $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$ at 76–300 K based on measurements of magnetic susceptibility of the phases. The Neel temperature, T_N, of interest was based on the temperature dependence of magnetization of the phases. It was shown that a local antiferromagnetic arrangement of the Fe^{3+} ions in $Fe_2V_4O_{13}$, $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$ is already involved at a temperature much higher than the Neel temperature, resulting from the cation–anion–cation superexchange between the Fe^{3+} ions with a d^5 configuration.

1. Introduction

Oxides as components of the Fe_2O_3–V_2O_5–MoO_3 system and phases that exist in two-component systems to build the three-component system have been an object of comprehensive studies for many years, initially on account of their catalytic properties. In a study of the mechanism of catalytic processes, a particularly important role is played, in addition to a knowledge of the structure and physico-chemical properties of the catalyst, by its magnetic properties [1, 2].

A literature survey has proved the basic magnetic properties of the oxides to be well known [3–5]. The magnetic properties of some phases existing in two-component systems, namely V_2O_5–MoO_3, Fe_2O_3–MoO_3 and Fe_2O_3–V_2O_5 are also known. The magnetic properties of phases existing in the V_2O_5–MoO_3 system, i.e. a solid solution of MoO_3 in V_2O_5, and those of the compound, $V_9Mo_6O_{40}$, are known mainly through the studies of Bielański *et al.* and Burzo *et al.* [6–9]. Both the solution and $V_9Mo_6O_{40}$ were also studied by electron paramagnetic resonance (EPR) [7–9]. The studies have permitted a model to be established for the solid solution and have shown that in $V_9Mo_6O_{40}$, one in nine of the vanadium atoms is in the form of V^{4+} ions [7, 8].

A number of works have dealt with $Fe_2(MoO_4)_3$, a compound existing in the Fe_2O_3–MoO_3 system [10]. The complete magnetic structure of the compound at 2–800 K is known well [11, 12].

A solid solution of Fe_2O_3 in V_2O_5 occurring in Fe_2O_3–V_2O_5 was studied spectroscopically by Burzo *et al.* [13] and Abdullaev *et al.* [14]. The magnetic properties of $FeVO_4$ [15, 16], of other compounds, besides $Fe_2V_4O_{13}$, existing in the Fe_2O_3–V_2O_5 system, are also known [17]. On the other hand, the magnetic properties of $Fe_2V_4O_{13}$, of a solid solution of MoO_3 in $Fe_2V_4O_{13}$, of $FeVMoO_7$ [18] and of $Fe_4V_2Mo_3O_{20}$ [19] existing in the Fe_2O_3–V_2O_5–MoO_3 system have been studied exclusively by Kuriata *et al.* [20–24]. The temperature dependence of magnetic susceptibility of $Fe_2V_4O_{13}$ and of a solid solution of MoO_3 in $Fe_2V_4O_{13}$ has been established [20]. $Fe_2V_4O_{13}$, a solid solution of MoO_3 in that compound, as well as $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$, have also been investigated by EPR [21–24], and the phases were found to be antiferromagnetic with a single axis. Their Neel temperature was also determined [21–24]. However, the dependence of magnetic susceptibility and magnetization of $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$ on the temperature and magnetization of $Fe_2V_4O_{13}$ at 4.2–300 K have not yet been studied.

2. Experimental procedure

Preparations, prepared from Fe_2O_3 and V_2O_5 (both reagent grade) and from MoO_3 produced by thermal decomposition of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ at 150–450 °C in air, were used for measurements of magnetic susceptibility and intensity of magnetization. $Fe_2V_4O_{13}$ was obtained from a mixture of Fe_2O_3 and V_2O_5 heated at a molar ratio of 1:2 at 610–620 °C in three 72 h cycles. $FeVMoO_7$ was synthesized from a mixture of Fe_2O_3, V_2O_5 and MoO_3 heated at a molar ratio 1:1:2 under the following conditions: 500 °C for 24 h, 550 °C for 48 h, and 600 °C for 24 h. Next, $Fe_4V_2Mo_3O_{20}$ was obtained from a mixture of Fe_2O_3, V_2O_5 and MoO_3 heated at a molar ratio 2:1:3 at 600 °C for 24 h, 650 °C for 24 h, and 700 °C for 72 h. X-ray powder diffraction (XRD) showed all the preparations obtained to be monophase. On the differential thermal analysis (DTA) curves of the phases obtained only effects related to the melting of the phases were recorded.

Measurements of magnetic susceptibility were accomplished by the Faraday method using a magnetic

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balance. Dy_2O_3 was used as a standard sample. The measurements were made at 76–300 K, in steps of 5 K. The fraction of diamagnetic susceptibility in the magnetic susceptibility determined experimentally was calculated using the Slater–Angus method. Measurements of magnetization were made using induction, at 4.2–300 K in an induction field of 10 T.

3. Results and discussion

The magnetic susceptibility results for $Fe_2V_4O_{13}$, $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$ at 76–300 K are shown in the form of a relation $1/\chi_M = f(T)$ in Fig. 1. Table I shows values of the Curie constant, effective magnetic moment, the Weiss constant and the spectroscopic splitting factor for the Fe^{3+} ion, all based on the results obtained for the compounds examined.

It follows from Fig. 1 that the molar magnetic susceptibilities of $Fe_2V_4O_{13}$, $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$ fulfil the Curie–Weiss law. Negative values of the Weiss constant, θ, imply that the magnetic moments of Fe^{3+}, are completed antiferromagnetically in the three compounds. In addition, Table I shows that the effective magnetic moments of the Fe^{3+} ions in the compounds under study stray from the theoretical value, $\mu_{eff(theor.)} = 5.92\ \mu B$, computed for the $^6S_{5/2}$ state of Fe^{3+}. Despite the discrepancy, they indicate the presence of five unpaired $3d$ electrons in the structure of the iron ions. The values of the spectroscopic splitting factor, g, for the Fe^{3+} ions in the compounds of interest explicitly stray from the theoretical value corresponding with the ground state, $^6S_{5/2}$, of Fe^{3+}, i.e. $g = 2.0023$ upwards. The Δg observed are high enough not to be attributed exclusively to a spin–orbital interaction that leads to a rather small collapse of the LS coupling giving rise to a small element of the excited state in the ground state.

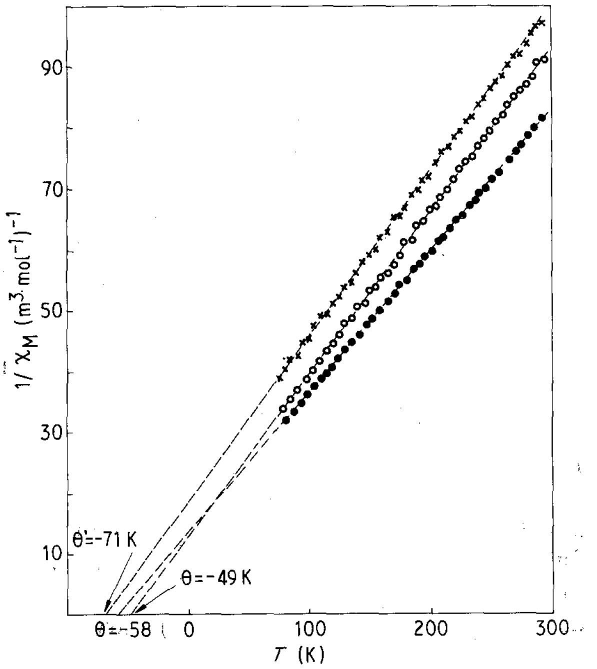

Figure 1 Temperature dependence of the inverse molar magnetic susceptibility for (●) $Fe_2V_4O_{13}$, (○) $FeVMoO_7$ and (×) $Fe_4V_2Mo_3O_{20}$.

The effect of the excited state impurity does not, in general, involve changes in the values of the spectroscopic splitting factor beyond 0.0003 [25]. It is known from the literature survey that considerably high Δg values are often observed for compounds in which the bonding of a paramagnetic ion with an oxygen ion is of a distinctly covalent character [26, 27]. The observations imply that the Δg values observed arise from a considerable share of a covalent bond in the Fe–O bonding in the compound under study.

Fig. 2 shows results from the magnetization measurements made for $Fe_2V_4O_{13}$, $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$ in a field with a magnetic induction of 10 T at 4.2–300 K; from the results the Neel temperature, T_N, may be determined for the compounds: T_N for $FeVMoO_7$ is about 14 K, that for $Fe_2V_4O_{13}$ is confined within 6–8 K, whereas that for $Fe_4V_2Mo_3O_{20}$ is below 4.2 K. The T_N values established differ considerably from the T_N calculated by the EPR method [21, 23, 24].

Fig. 3 shows a molar magnetization for the Fe^{3+} ions in the $^6S_{5/2}$ ground state calculated according to the Brillouin formula describing an ideal intensity

TABLE I Some magnitudes typical of magnetic properties of $Fe_2V_4O_{13}$, $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$

Compound	C (K mol^{-1})	θ (K)	μ_{eff} (μB)	g
$Fe_2V_4O_{13}$	4.318	−58	5.90	1.9946
$FeVMoO_7$	3.760	−49	5.50	1.8594
$Fe_4V_2Mo_3O_{20}$	3.766	−71	5.51	1.8627

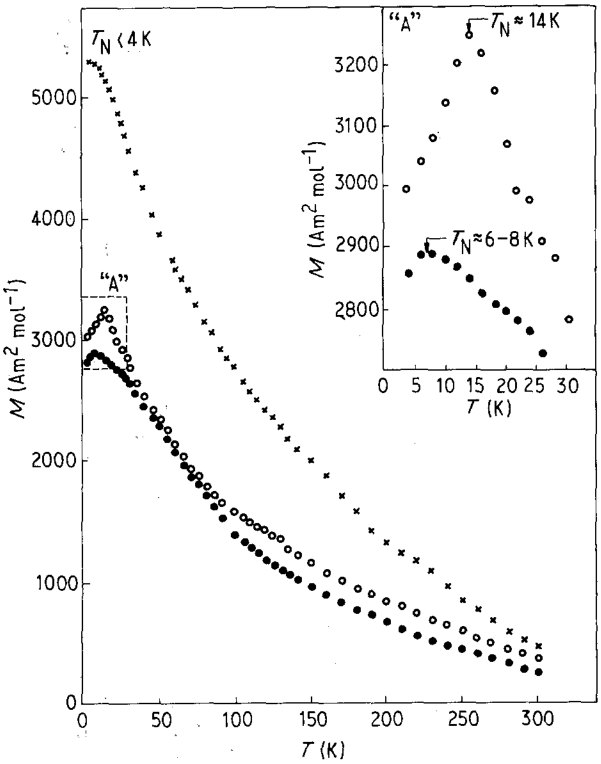

Figure 2 Temperature dependence of molar magnetization for (●) $Fe_2V_4O_{13}$, (○) $FeVMoO_7$ and (×) $Fe_4V_2Mo_3O_{20}$ at an applied field of $B = 10$ T.

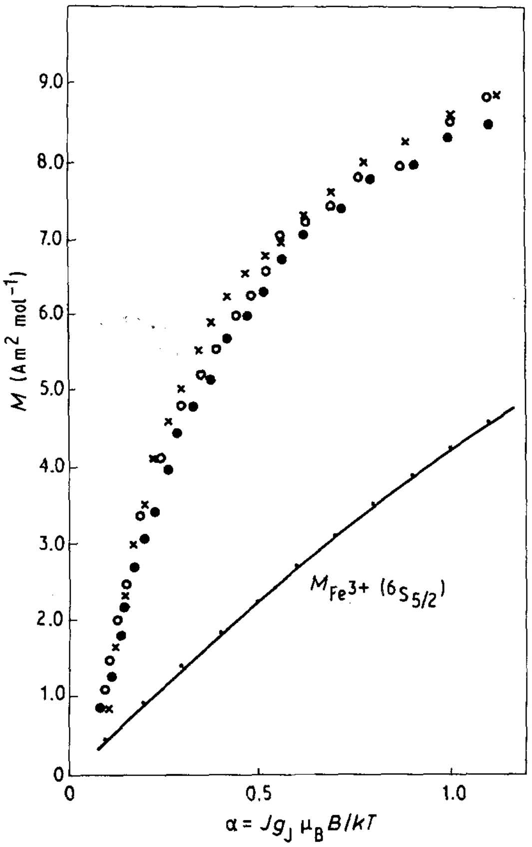

Figure 3 α-dependence of molar magnetization for the Fe^{3+} ions in the $^6S_{5/2}$ ground state and of the experimental molar magnetization values for (●) $Fe_2V_4O_{13}$, (○) $FeVMoO_7$ and (×) $Fe_4V_2Mo_3O_{20}$.

of magnetization of a paramagnetic in the function of $\alpha = Jg\mu_B B/kT$ [28]; the figure also shows the molar intensities of magnetization of $Fe_2V_4O_{13}$, $Fe_4V_2Mo_3O_{20}$ and $FeVMoO_7$ established experimentally, after normalizing their values to 10 Am^2 mol^{-1} at 30–300 K, i.e. at temperatures much higher than the Neel temperature of those phases. The theoretical magnetization of the Fe^{3+} ions has been calculated taking a value $g = 2.0023$ for the spectroscopic splitting factor, whereas the values of the molar magnetization in the function α for the compounds under study have been based on the experimental values of g (Table I). The relations shown in Fig. 3 imply that in the paramagnetic range ($T > T_N$), the experimentally established molar magnetization of the Fe^{3+} ions in $Fe_2V_4O_{13}$, $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$ markedly strays from the theoretical magnitude of the magnetization of Fe^{3+} in the $^6S_{5/2}$ ground state, showing the phases not to be "pure" paramagnetics. Because it has been impossible to describe the magnetization changes in those phases in the function α by the Brillouin formula, it is suggested that a local interaction, antiferromagnetic in character, of the iron ions in the compounds under study occurs at a temperature much higher than the magnetic transformation temperature of the phases, as proved from the temperature dependence of the EPR line width established by the EPR method [21, 23, 24]. Fig. 4 shows the dependence for Fe^{3+} in $Fe_2V_4O_{13}$ [21]. The dependence in question for $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$ appears to be similar [23, 24]. According to theory [29], the ΔB_{p-p} breadth of the EPR lines in the paramagnetic range and a wide temperature range is constant, not increasing monotonically with decrease over a high range of temperature, as has been noticed with the compounds studied [21, 23, 24].

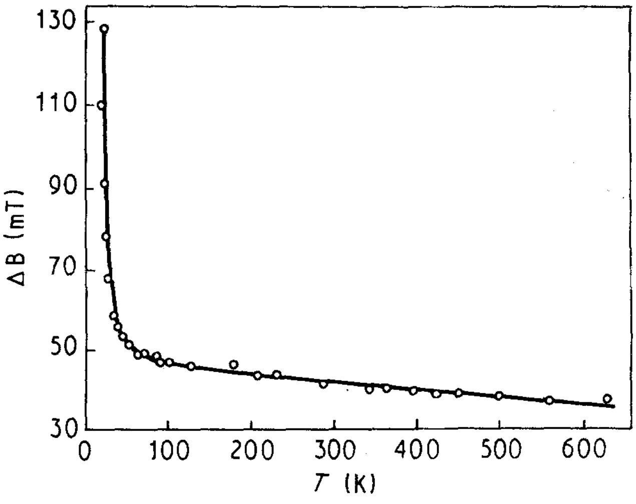

Figure 4 Temperature dependence of the EPR line width for $Fe_2V_4O_{13}$.

The occurrence of a local antiferromagnetism at a temperature much higher than the magnetic transformation temperature can be refined by the existence of a strong exchange interaction between Fe^{3+} and the oxygen ions. The existence of a local antiferromagnetism obliquely indicates the presence of the Fe–O–Fe bonds in the compounds and, at the same time, explains marked discrepancies between the measured and theoretical values of the Fe^{3+} spectroscopic splitting factor.

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