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Metamagnetism in the $Cr_2V_{4-x}Mo_xO_{13+0.5x}$ solid solutions

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Magnetic investigations were carried out in the temperature range 4.2–300 K, in stationary magnetic fields up to 14 T and in the pulsed magnetic fields up to 38 T on polycrystalline solid solutions of $Cr_2V_{4-x}Mo_xO_{13+0.5x}$ with $x=0.0$, 0.22, 0.29, 0.35, 0.42, and 0.5. Antiferromagnetic ordering with a Néel temperature $T_N \approx 13$ K and the paramagnetic Curie-Weiss temperature $\Theta_{CW} \approx -22$ K was established for all samples. Additionally two metamagnetic thresholds were observed for samples with $x=0.0$, 0.29, and 0.5 in stationary magnetic fields up to 14 T. All samples have low effective magnetic moments which are far from the saturation expected for the spin-only $2Cr^{3+}$ moment of $6\mu_B$. The metamagnetic state is explained in terms of a large anisotropy, an asymmetric cation-anion-cation superexchange interaction, and an additional superexchange interaction involving the nonmagnetic tetrahedral vanadate and molybdate groups.

I. INTRODUCTION

The solid solutions of the type $Cr_2V_{4-x}Mo_xO_{13+0.5x}$ are very interesting because they can play a role both as active and selective catalysts in oxidation processes. Differential thermal analysis (DTA) and x-ray investigations[1] of the system Cr_2O_3-V_2O_5-MoO_3 showed that MoO_3 forms limited solid solutions with $Cr_2V_4O_{13}$. The maximum solubility being about 16%. The structure of $Cr_2V_4O_{13}$ is not yet known, however, the solid solution samples with $x=0.0$, 0.22, 0.29, 0.35, 0.42, and 0.5 appeared to be single phase.[1] From electron paramagnetic resonance (EPR) measurements[2] the Néel temperature is $T_N=7$ K and the g factor is 1.97 for the $Cr_2V_4O_{13}$ matrix.

Measurements[3] of the electrical resistivity, the Seebeck effect, and the UV/VIS absorption as carried out on $Cr_2V_{4-x}Mo_xO_{13+0.5x}$ solid solutions showed that (1) they are insulators at room temperature, (2) at about 700 K a phase transition from an insulating to a semiconducting state takes place, (3) a change of the type of the electrical conductivity (from n to p) takes place with the increase of Mo concentration, (4) the absorption edge shifts to higher wavelengths which is probably caused by the reduction of Cr^{3+} to Cr^{2+}.

In this paper an attempt is made to explain the magnetic properties in the $Cr_2V_{4-x}Mo_xO_{13+0.5x}$ solid solutions. For that the magnetic susceptibility and the magnetization were measured in medium stationary magnetic fields (up to 0.6 T), in high magnetic stationary fields (up to 14 T) and in high pulsed magnetic fields (up to 38 T). A model based on superexchange interaction is discussed.

II. EXPERIMENT

A. Preparation

The samples of the solid solutions $Cr_2V_{4-x}Mo_xO_{13+0.5x}$ ($x=0.0$, 0.22, 0.29, 0.35, 0.42, and 0.5) were kindly provided by Walczak and Filipek. All the details concerning the preparation techniques are described elsewhere.[1,4–6]

B. Measurements

The magnetic susceptibility and the magnetization of the solid solutions were investigated with the aid of the following techniques: (1) medium stationary magnetic fields up to 0.6 T within a temperature range 77–300 K using a Faraday-Obuszko type of magnetic balance, (2) medium stationary magnetic fields up to 1 T within a temperature range 4.2–100 K using an induction magnetometer, (3) high magnetic stationary fields up to 14 T at 4.2 K using an induction magnetometer, (4) high pulsed magnetic fields up to 38 T at 4.2 K using the induction method.

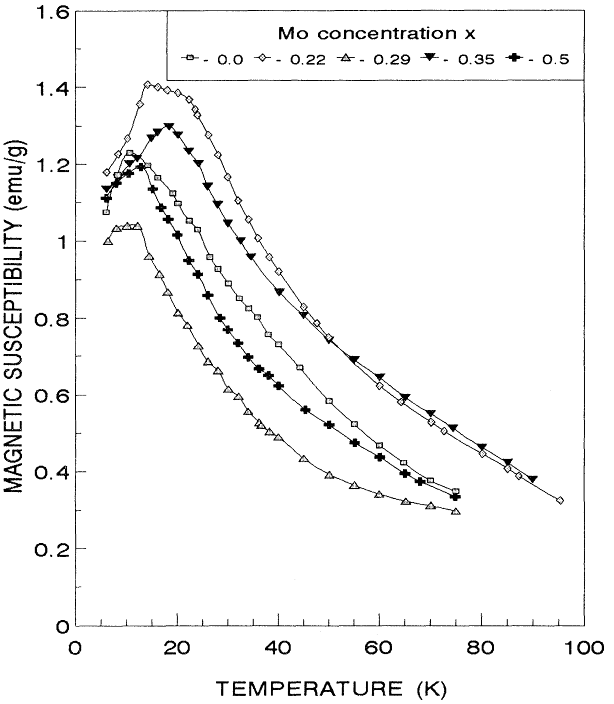

FIG. 1. Magnetic susceptibility vs temperature for $Cr_2V_{4-x}Mo_xO_{13+0.5x}$ solid solutions with $x = 0.0$, 0.22, 0.29, 0.35, and 0.5. Magnetic field: 1T.

III. RESULTS

A. Néel temperature measurements

Figure 1 shows the magnetic susceptibility as a function of temperature in the range 4.2–100 K for Mo concentration $x = 0.0$, 0.22, 0.29, 0.35, and 0.5; the applied magnetic field is 1 T. The behavior of all the samples is typical of an antiferromagnet except for a plateau introducing magnetic ions range ordering instead of a Néel point T_N. It suggests that the antiferromagnetic structure is more complex (noncollinear, canted, or clustered). However, we cannot exclude additional ferromagnetic couplings. Eventually, we have an order-order transition following the order-disorder transitions at T_N. The value of Néel temperature T_N has been taken at the temperature where the derivative of the magnetic susceptibility equals zero. Then, the Néel temperatures are observed between 10 and 18 K (see Table I). The largest T_N have those samples which do not show the metamagnetic transitions.

TABLE I. Experimental data of the $Cr_2V_{4-x}Mo_xO_{13+0.5x}$ solid solutions: the Néel temperature T_N, the paramagnetic Curie-Weiss temperature Θ_{CW}, the Curie molar constant C_M, the effective moment per molecule μ_{eff}, and the magnetic moment μ per molecule at 4.2 K and in a magnetic field of 38 T.

x	T_N (K)	Θ_{CW} (K)	C_M (K mol^{-1})	μ_{eff} (μ_B)	μ (μ_B)
0.00	10	−23	3.03	4.92	2.68
0.22	14	−22	2.42	4.40	3.41
0.29	11	−15	2.52	4.49	2.08
0.35	18	−30	2.60	4.56	3.47
0.42		−23	2.74	4.68	3.32
0.50	12	−17	2.91	4.82	3.25

B. Magnetization curves

Figure 2 shows the magnetization versus field curves for stationary magnetic fields up to 14 T at 4.2 K. The steps in the $M(B)$ curves for $x = 0.0$, 0.29, and 0.5 suggest metamagnetic behavior; they are missing for $x = 0.22$ and 0.35, indicating antiferromagnetism for all fields. The first metamagnetic threshold is observed at $B_1 = 1.1$, 2.1, and 1.2 T for the samples with $x = 0.0$, 0.29, and 0.5, respectively. The second metamagnetic threshold B_2 decreases with the increase of Mo concentration from $B_2 = 3.7$ T for $x = 0.0$, to 3.2 T for $x = 0.29$ and 1.6 T for $x = 0.5$.

Figure 3 shows typical magnetization versus field curves when a magnetic field pulse up to 38 T is applied for different Mo concentration also at 4.2 K. The initial linear slope suggests an antiferromagnetic ordering of the chromium ions. The maximum magnetic moment at 38 T calculated per molecule does not exceed the value of $3.5\mu_B$ for any sample (see Table I). This is significantly lower as the spin-only $2Cr^{3+}$ moment of $6\mu_B$.

C. Paramagnetic susceptibility

Figure 4 shows the reciprocal molar susceptibility as a function of temperature (in the range 77–300 K) for Mo

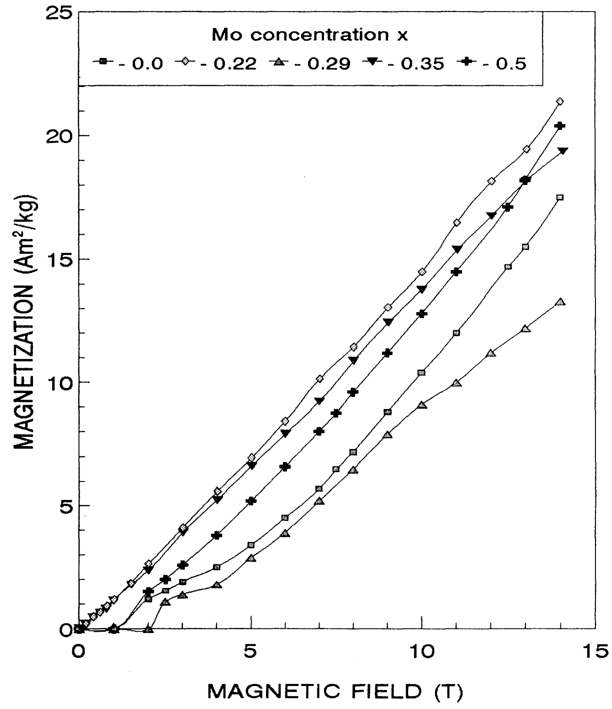

FIG. 2. Magnetization vs field curves using stationary magnetic field for $Cr_2V_{4-x}Mo_xO_{13+0.5x}$ solid solutions with $x = 0.0$, 0.22, 0.29, 0.35, and 0.5 at 4.2 K.

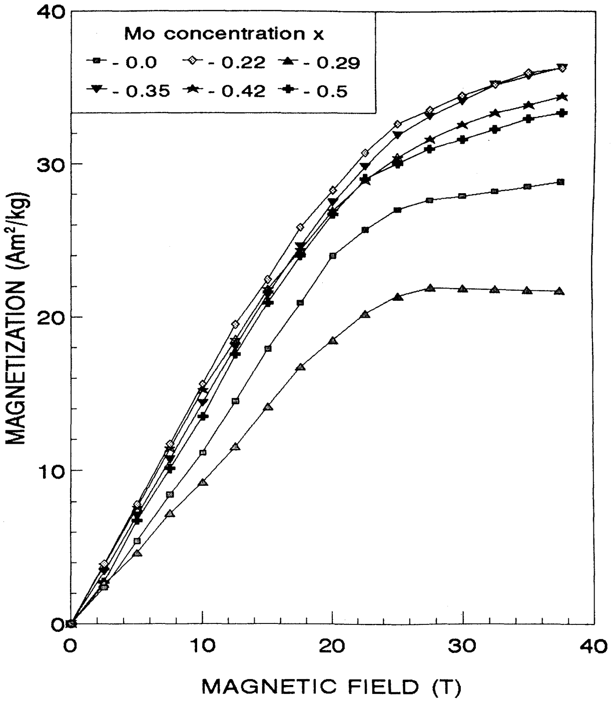

FIG. 3. Magnetization vs field curves using magnetic field pulses for $Cr_2V_{4-x}Mo_xO_{13+0.5x}$ solid solutions with $x=0.0$, 0.22, 0.29, 0.35, 0.42, and 0.5 at 4.2 K.

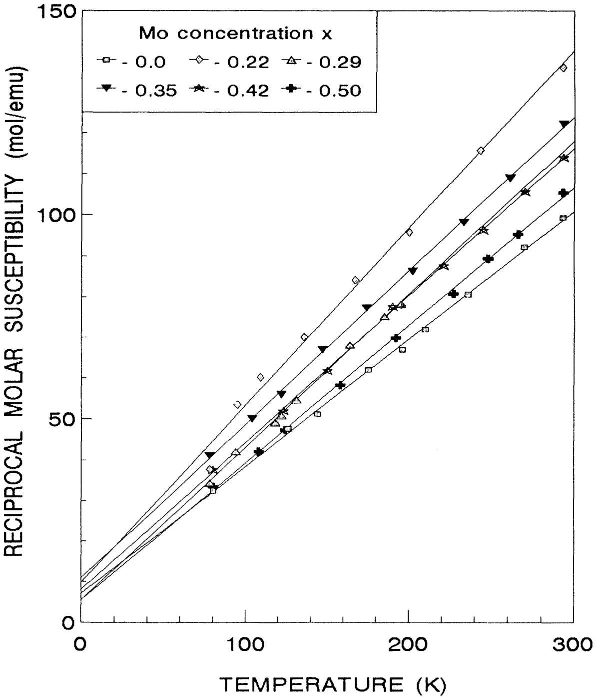

FIG. 4. Reciprocal molar susceptibility against temperature in the $Cr_2V_{4-x}Mo_xO_{13+0.5x}$ solid solutions with $x=0.0$, 0.22, 0.29, 0.35, 0.42, and 0.5; magnetic field: 0.6 T.

concentrations $x=0.0$, 0.22, 0.29, 0.35, 0.42, and 0.5; the magnetic field used is 0.6 T. The paramagnetic Curie-Weiss temperature Θ_{CW} was determined for all samples by extrapolation of the linear part of the reciprocal molar susceptibility versus temperature to the horizontal axis. Consistent with antiferromagnetic ordering, all paramagnetic Curie-Weiss temperatures have negative signs and their values range from -15 to -30 K. The molar Curie constants C_M have been determined from the slope of the $\chi(T)$ curves. The largest values of C_M per molecule is observed for the sample with $x=0.0$. With the increase of the Mo concentration the molar Curie constant increases from 2.42 for $x=0.22$–2.91 K mol^{-1} for $x=0.5$ (see Table I). The effective magnetic moment has been determined using $\mu_{\text{eff}} = (3k_BC_M/N_A\mu_B^2)^{1/2}$ $(\approx 2.828\sqrt{C_M})$ where C_M is the molar Curie constant; N_A, Avogadro's number; k_B, Boltzmann's constant; and μ_B, the Bohr magneton. The effective moment for $x=0$ is $\mu_{\text{eff}}=4.92\mu_B$; it drops for $x>0$ and increases again from 4.4 for $x=0.22$ to $4.82\mu_B$ for $x=0.5$ (see Table I). All the values of the effective magnetic moments are too low in comparison with the theoretical value for $2Cr^{3+}$ ions $(5.477\mu_B)$ which should exist in a high-spin state (orbital singlet) $^4F_{3/2}$. The experimental data are summarized in Table I.

IV. DISCUSSION

A. Magnetic interactions

The above results suggest that the $Cr_2V_{4-x}Mo_xO_{13+0.5x}$ solid solutions are antiferromagnets with a low Néel temperature $T_N \approx 13$ K and the negative value of a paramagnetic Curie-Weiss temperature $\Theta_{CW} \approx -22$ K. For all samples the inequality $0<|-T_N/\Theta_{CW}|<1$ is observed. This could arise from two competing inter- and intralattice negative magnetic interactions. However, we cannot also exclude additional ferromagnetic couplings. Similar anomalous shapes of the magnetization curves in the vicinity of the Néel temperature for $FeVO_4$ and $CrVO_4$ have been found.[7] In this case they have been connected with the magnetically ordered microscopic regions.

The nature of antiferromagnetism in the $Cr_2V_{4-x}Mo_xO_{13+0.5x}$ solid solutions may be caused by the strong superexchange interactions along a path through the nonmagnetic groups, Cr-O-O-Cr, or more complex, Cr-O-V-O-Cr, as was suggested for the orthorhombic $CrVO_4$ antiferromagnet.[8] In our case the nonmagnetic molybdate groups (MoO_4) also have to be considered. The lower values of the effective magnetic moments in comparison with the theoretical high spin value for $2Cr^{3+}$ ions can suggest that eventually, some of the Cr^{3+} ions are tetrahedrally coordinated to oxygen. In the tetrahedral coordination Cr^{3+} ions exist in the low spin state.

B. Metamagnetic transitions

Metamagnetic transitions are observed for the samples which have the lowest magnetic moment in the magnetic field of 38 T (see Table I). However, all samples have strongly lower magnetic moments in comparison to the expected saturation values. This makes room for several metamagnetic thresholds when larger magnetic fields are applied leading to a multistage metamagnetic structure. The nature of the metamagnetism existing in the solid solutions under study has been connected with the strong anistropy[9] which usually accompanies crystal structures with low symmetry. In our case the late saturation of the magnetization suggests a large magnetic anisotropy in the $Cr_2V_{4-x}Mo_xO_{13+0.5x}$ solid solutions. Also in the structures with low symmetry the magnetic ions are often joined to create a complex chain of six-sharing polyhedra as it was observed in triclinic $FeVO_4$.[10] If these chains exist they can be additionally joined by the tetrahedra of vanadate groups (VO_4) (Ref. 10) and by the tetrahedra of the molybdate groups (MoO_4).

Another explanation for the metamagnetic states is connected with asymmetric superexchange in the cation-anion-cation chain or involving the nonmagnetic tetrahedral groups VO_4 and MoO_4. Asymmetric exchange usually leads to a small canting of the sublattices.[11]

V. CONCLUSION

Complex magnetic structures, the lack of complete saturation and the low crystal symmetry are typical for compounds and solids solutions which show catalytic behavior.[12,13] Eventually the study of the magnetic properties in such materials will help to understand the catalytic mechanism.

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[1] J. Walczak and E. Filipek, Thermochim. Acta **133**, 67 (1988).

[2] J. Kuriata, L. Sadłowski, J. M. Baker, M. Newton, J. Walczak, and E. Filipek (unpublished).

[3] T. Grón, H. Duda, J. Krok-Kowalski, J. Walczak, E. Filipek, A. Wyrostek, and K. Bärner, Radia. Eff. Def. Solids (to be published).

[4] J. Walczak and E. Filipek, J. Therm. Anal. **35**, 69 (1989).

[5] J. Walczak, and E. Filipek, Thermochim. Acta **161**, 239 (1990).

[6] J. Walczak and E. Filipek, Thermochim. Acta **173**, 235 (1990).

[7] Vad. I. Surikov, I. I. Miller, Val. I. Surikov, V. N. Lisson, L. A. Ugodnikova, and E. M. Yarosh, Fiz. Tverd. Tela (Leningrad) **21**, 1582 (1979) [Sov. Phys. Solid State **21**, 913 (1979)].

[8] B. C. Frazer and P. J. Brown, Phys. Rev. **125**, 1283 (1962).

[9] D. Gignoux, in *Magnetic Properties of Metallic Systems,* edited by R. W. Cahn, P. Hassen, and E. J. Kramer (VCH, Weinheim, 1993), Vol. 3A, Part I, p. 384.

[10] B. Robertson and E. Kostiner, J. Solid State Chem. **4**, 29 (1972).

[11] T. Moriya, Phys. Rev. **120**, 91 (1960).

[12] R. Maliński, J. Gallus-Olender, and T. Kubicka, React. Kinet. Catal. Lett. **10**, 219 (1979).

[13] P. Forzatti, C. M. Mari, and P. Villa, Mater. Res. Bull. **22**, 1593 (1987).