

Magnetic Properties of Ti_3O_5 with Chromium Additions

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Dedicated to Professor Paul Hagenmuller on occasion of his 65. birthday

Abstract. Magnetic susceptibility measurements were used to study solid solutions $Ti_{3-x}Cr_xO_5$ ($0 \leq x \leq 0.17$). Contributions to magnetic susceptibility for the α -phase were defined by the statistical analysis of the experimental data. A conclusion was made on the varying character of exchange interactions in α - $Ti_{3-x}Cr_xO_5$ with increasing Cr content. In the present work, the information given indicates that Cr stabilizes the high-temperature α - Ti_3O_5 and decreases the temperature of semiconductor-metal phase transition. Magnetic properties of low-temperature β - Ti_3O_5 phase with chromium addition are shown to be explained by the existence of exchange-coupled pairs $Ti^{3+}-Cr^{3+}$.

Magnetische Eigenschaften von Ti_3O_5 mit Chrom-Zusätzen

Inhaltsübersicht. Magnetische Messungen wurden zur Untersuchung der festen Lösungen $Ti_{3-x}Cr_xO_5$ ($0 \leq x \leq 0,17$) ausgeführt. Anteile zur magnetischen Suszeptibilität der α -Phase werden mittels statistischer Analyse der experimentellen Daten erklärt. Rückschlüsse auf den sich ändernden Charakter der Austauschwechselwirkungen im α - $Ti_{3-x}Cr_xO_5$ mit steigendem Cr-Gehalt werden gezogen. Die Daten zeigen, daß Chrom die Hochtemperatur- α - Ti_3O_5 -Phase stabilisiert und die Temperatur für den Halbleiter-Metall-Übergang senkt. Die magnetischen Eigenschaften der Tieftemperatur- β -Phase können durch die Existenz von Austausch-Paaren $Ti^{3+}-Cr^{3+}$ erklärt werden.

The semiconductor-metal phase transition accompanied by a sharp change of electric, magnetic, structural, and other characteristics, occurs in Ti_3O_5 oxide at 450 K. For better understanding the nature of the phase transition in the given oxide it is interesting to consider some data on the properties changes of Ti_3O_5 under the influence of different factors including doping.

Solid solutions $Ti_{3-x}Cr_xO_5$ ($0 \leq x \leq 0.17$) were studied in present work. Samples were prepared according to ceramic technology. The main method used was the magnetochemical one: magnetic susceptibility was measured by the Faraday method in the temperature range 77 to 1100 K. Fig. 1 shows the polytherms of magnetic susceptibility of $Ti_{3-x}Cr_xO_5$.

The experimental data analysis shows that the magnetic susceptibility of the low-temperature (β) phase of solid solutions is well described by the equations:

$$\chi_{\beta} = A + C(T - \Theta)^{-1}, \quad (1)$$

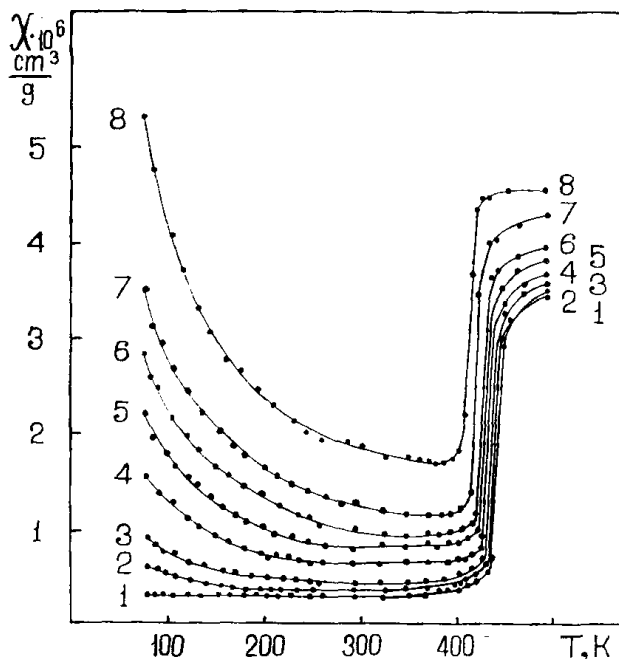


Fig. 1

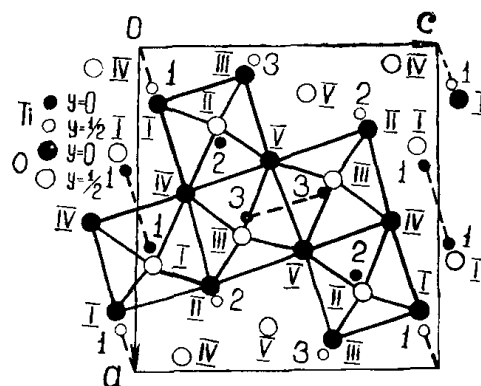


Fig. 2

Fig. 1 Polytherms of magnetic susceptibility for $\beta\text{-Ti}_{3-x}\text{Cr}_x\text{O}_5$.

1. $x = 0$, 2. $x = 0.005$, 3. $x = 0.01$, 4. $x = 0.02$,
5. $x = 0.03$, 6. $x = 0.04$, 7. $x = 0.05$, 8. $x = 0.08$

Fig. 2 Crystal structure of the low-temperature modification of Ti_3O_5 [2]. Projection on plane ac .
1, 2, 3 — Ti positions, I, II, III, IV, V — O positions.

where A—the temperature independent term including the diamagnetic contribution and paramagnetism of Van Vleck, C—the Curie constant, Θ —the Weiss constant.

The parameters of this equation as well as the magnetic moment per a formula unit of $\text{Ti}_{3-x}\text{Cr}_x\text{O}_5$, obtained by a statistical treatment of the experimental data are given in Table 1.

Table 1 Parameters of the Curie-Weiss equation for $\beta\text{-Ti}_{3-x}\text{Cr}_x\text{O}_5$

x in $\text{Ti}_{3-x}\text{Cr}_x\text{O}_5$	$A \cdot 10^6$, cm^3/mol	Θ , K	C, $\text{cm}^3/\text{mol} \cdot \text{K}$	μ , μ_B	α -phase fraction
0	52.1	-5	0.00153	0.1105	—
0.005	44.8	-4	0.00727	0.2411	—
0.010	48.7	-6	0.01278	0.3198	—
0.020	44.5	-11	0.02598	0.4559	—
0.030	47.9	-7	0.03761	0.5686	—
0.040	56.6	-8	0.0493	0.6281	—
0.050	64.4	-13	0.0644	0.7182	0
0.080	73.4	-9	0.0959	0.9759	0
0.100	81.4	-33	0.1676	1.1570	0.161
0.120	311	-55	0.2848	1.5090	0.640
0.150	529	-33	0.3013	1.5530	0.848
0.170	774	-113	0.2388	1.382	0.883

To explain magnetic properties of pure Ti_3O_5 one can use a model suggested by MULAY and DANLEY [1]. In the low-temperature modification there exist three crystallographically non-equivalent Ti positions: Ti1, Ti2, and Ti3 (Fig. 2). Positions Ti1 and Ti3 are occupied by Ti^{3+} ions, and those of Ti2 by Ti^{4+} ions. The interionic distance of the three-valent Ti are so that Ti1—Ti1 and Ti3—Ti3 pairs are formed. Ti^{3+} ions in pairs are coupled with a strong antiferromagnetic interaction of the intramolecular type similar to that which is observed in coordination compounds. This interaction decreases the magnetic susceptibility of the β -phase compared with the metallic α -phase, and causes the absence of the orientational paramagnetism connected with Ti^{3+} ions in the β -phase of stoichiometric Ti_3O_5 . On the $\beta \rightarrow \alpha$ transition the interatomic distances in Ti are averaged, the oxide transforms into the metal state and its magnetic susceptibility is described by a free electron gas model.

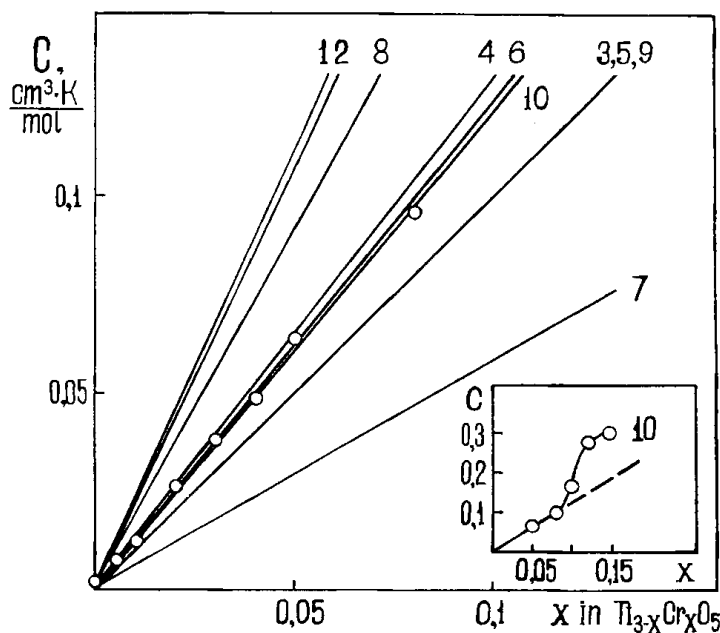


Fig. 3 Concentration dependences of experimental, C_{exp} , and theoretical, C_{th} , Curie constants for $\beta-Ti_{3-x}Cr_xO_5$.

1. $C_{th} = 2.250x$	$Cr_{Ti1, Ti3}^{3+}$	A-pairs are not formed
2. $C_{th} = 2.125x$	$Cr_{Ti1, Ti2, Ti3}^{3+}$	A-pairs are not formed
3. $C_{th} = x$	$Cr_{Ti1, Ti3}^{3+}$	A-pairs are formed
4. $C_{th} = 1.292x$	$Cr_{Ti1, Ti2, Ti3}^{3+}$	A-pairs are formed
5. $C_{th} = x$	Cr_{Ti2}^{3+}	
6. $C_{th} = 1.250x$	$Cr_{Ti1, Ti2, Ti3}^{4+}$	B-pairs are not formed
7. $C_{th} = 0.583x$	$Cr_{Ti1, Ti2, Ti3}^{4+}$	B-pairs are formed
8. $C_{th} = 1.833x$	$Cr_{Ti1, Ti3}^{3+}, Cr_{Ti2}^{4+}$	A-pairs are not formed
9. $C_{th} = x$	$Cr_{Ti1, Ti3}^{3+}, Cr_{Ti2}^{4+}$	A-pairs are formed
10. $C_{exp} = 1.205x$		

The nonzero value of Curie constant obtained for pure Ti_3O_5 (Table 1) is due to presence of eigndefects in the oxide causing the break of some $\text{Ti}^{3+}-\text{Ti}^{3+}$ pairs. Uncoupled Ti^{3+} ions (3 d¹) are paramagnetic centres. They amount to about 0.1% of stoichiometric content of the three-valent Ti in Ti_3O_5 . When Ti_3O_5 is doped with Cr, a regular increase of C and μ occurs. This indicates the formation of a large number of paramagnetic centres. Fig. 3 shows the experimental dependence of the Curie constant on concentration for the β -phase of solid solution as well as the theoretical relations $C_{\text{th}}(x)$, calculated for a number of models

$$C_{\text{th}} = 0.125x \sum_i n_i \mu_i^2 \quad (2)$$

where μ_i — the magnetic moment of one paramagnetic centre; n_i — a number of such centres in a formula unit $\beta\text{-Ti}_{3-x}\text{Cr}_x\text{O}_5$. The substitution of Ti by the three- and four-valent Cr is considered. Besides, the possibility of the formation of exchange-coupled $\text{Ti}^{3+}-\text{Cr}^{4+}$ and $\text{Ti}^{3+}-\text{Cr}^{3+}$ pairs is taken into account. $\text{Ti}^{3+}-\text{V}^{3+}$ pairs were described by us [3]. In both cases one Ti electron and one Cr electron participate in the metal-metal bond, and the remaining two electrons and one d-electron of Cr, respectively, contribute to paramagnetism. The substitution of Ti by Cr in Ti2 positions which don't participate in the metal-metal bond, leads to appearance of $\text{Cr}_{\text{Ti2}}^{3+}$ or $\text{Cr}_{\text{Ti2}}^{4+}$ paramagnetic centres. If Cr is in Ti1 or Ti3 positions, then in the case of bond formation the pair $\text{Ti}^{3+}-\text{Cr}^{3+}$ (3 d²) (is denoted "A") which in magnetic relation resembles Cr^{4+} , and the pair $\text{Ti}^{3+}-\text{Cr}^{4+}$ (3 d¹) (is denoted "B"), similar to Cr^{5+} , may be paramagnetic centres. When "A" or "B" pairs are not formed, then $\text{Cr}_{\text{Ti1,Ti2}}^{3+}$ ($\text{Cr}_{\text{Ti1,Ti3}}^{4+}$) and Ti^{3+} ion which is in the neighbour site, are the paramagnetic centres.

By means of a statistical treatment of the experimental data we obtained $C_{\text{exp}} = 1.205$ ($0 \leq x \leq 0.08$). The comparison of this relation with the theoretical ones (Fig. 3, models enumerated) gives the possibility to conclude that, firstly, variants 1, 2, 7, 8 may be not considered and, secondly, Cr in β -phase structure replaces Ti in all three crystallographic positions. The calculation shows that about 21.7% Cr is diluted in Ti2 positions. So, the final choice should be made between variants 4 and 6, that is to settle what oxidation extent has Cr in the lattice of Ti_3O_5 . Being Cr^{3+} it form pairs ("A"), in case of Cr^{4+} pairs ("B") are not formed. When Ti is replaced by Cr corresponding to variant 6, the number of paramagnetic centres connected with Ti^{3+} must increase because of the accumulation in the β -phase of the three-valent Ti ions released from the metal-metal bond as it occurs on doping of Ti_3O_5 with Zr and Sc [4]. In the case of $\text{Ti}_{3-x}\text{Cr}_x\text{O}_5$ there is observed the decrease of the integral intensity of the EPR signal connected to Ti^{3+} , with "x" increase in $\text{Ti}_{3-x}\text{Cr}_x\text{O}_5$ and its complete disappearance at $x > 0.05$. (In pure Ti_3O_5 the $\text{Ti}^{3+} - \square$ pair, where \square — metal vacancy [4], is responsible, in our opinion, for the EPR signal (g-factor 1.964). On the doping with Cr, the filling of metal vacancies occurs which causes the signal disappearance). So, the summation of experimental results is described best by variant "4", that is,

A-pairs which can't be obtained by the EPR method due to the short spin-lattice relaxation time, are the paramagnetic centres in the β -phase.

In Fig. 3 which shows the dependence of $C_{\text{exp}}(x)$, at $x = 0.09$, one can see the bend which indicates the appearance of the second phase impurity in samples studied. The X-ray phase analysis showed that this is a high-temperature modification (α) of doped oxide Ti_3O_5 . The existence of the α -phase in these samples can be determined by the EPR method as well. A wide symmetric line with $g=1.96$, the intensity of which rises with increased Cr concentration in $\text{Ti}_{3-x}\text{Cr}_x\text{O}_5$ is assigned to Cr^{3+} diluted in α -phase stabilised by the Cr presense to low temperatures (77 K). So, it may be concluded that Cr electrons are not collectivized at the $\beta \rightarrow \alpha$ phase transition but remain in localized states.

While calculating the electron effective masses in α - Ti_3O_5 phase [5] it is suggested that the susceptibility for the α -phase is temperature-independent. We think this model to be too crude. The analysis shows that the magnetic susceptibility of the α -phase is adequately described by the model

$$\chi_\alpha = A - BT^2, \quad (3)$$

where according to [6]:

$$A = \frac{12 m^* \mu_B^2}{h^2} \left(\frac{\pi}{3} \right)^{2/3} n^{1/3} \quad (4)$$

$$B = \frac{\pi^2}{12} \left(\frac{k}{\varepsilon_0} \right)^2 \cdot A, \quad (5)$$

where m^* -the electron effective mass, n -the free electron concentration, ε_0 -the Fermi energy.

By means of statistical treatment of experimental data for pure Ti_3O_5 in the 500 to 1100 K temperature range according to model (3) the following estimates were obtained: $A = (0.899 \pm 0.010) \cdot 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$, $B = (0.1960 \pm 0.0050) \cdot 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-2}$. Then, considering the diamagnetic correction we obtain $\varepsilon_0 = 0.175 \text{ eV}$ from (4) and (5). Taking into account that at the semiconductor-metal transition every formula unit Ti_3O_5 contributies two electrons into the conductivity region, one may evaluate the electron effective mass in the α -phase, $m^* = 29.34 m_e$.

To describe the temperature dependence of the magnetic susceptibility of the α -phase of $\text{Ti}_{3-x}\text{Cr}_x\text{O}_5$ solid solutions (Fig. 4) it is necessary to introduce a term proportional to T^{-1} being connected with localized moments. Assuming the additivity of metallic and ionic contributions, we introduce the model:

$$\chi_x = A - BT^2 + C(T - \Theta)^{-1}, \quad (6)$$

where C — the Curie constant, Θ — the Weiss constant. However, the simultaneous evaluation of four parameters (A , B , C and Θ) of the model (6), because of its nonlinearly, gave no stable estimates. As a result, the magnetic susceptibility analysis of $\text{Ti}_{3-x}\text{Cr}_x\text{O}_5$ solid solutions was carried out according to two submodels ("a" and "b") of model (6).

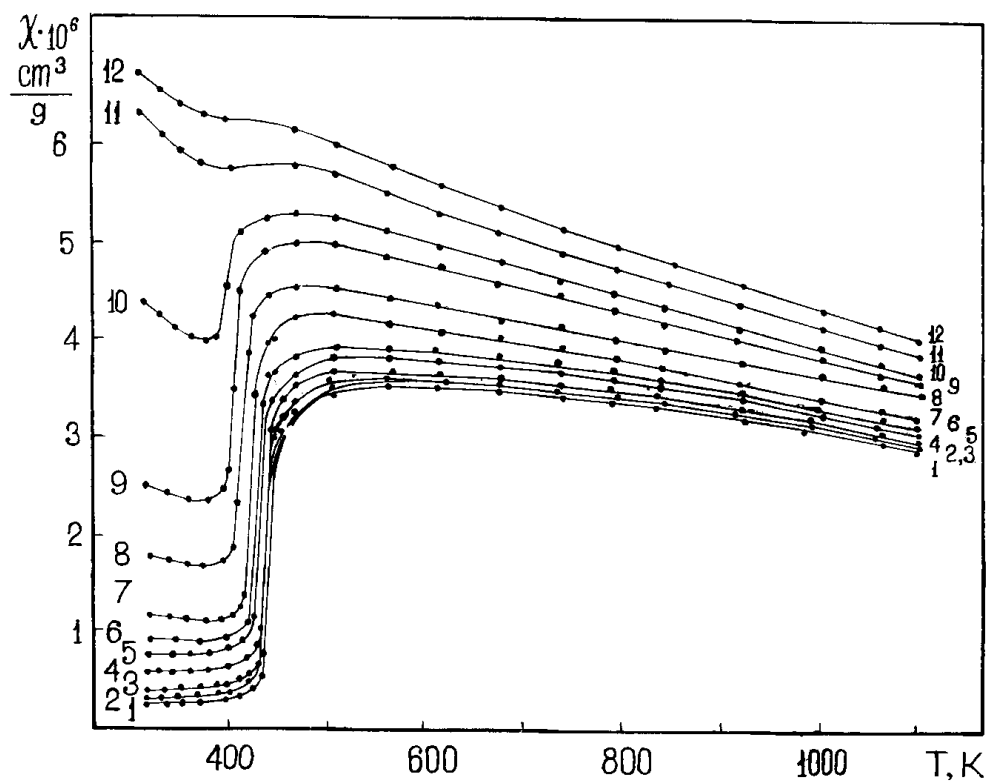


Fig. 4 Magnetic susceptibility polytherms for $\alpha\text{-Ti}_{3-x}\text{Cr}_x\text{O}_5$.

1. $x = 0$, 2. $x = 0.005$, 3. $x = 0.01$, 4. $x = 0.02$, 5. $x = 0.03$, 6. $x = 0.04$, 7. $x = 0.05$, 8. $x = 0.08$, 9. $x = 0.10$, 10. $x = 0.12$, 11. $x = 0.15$, 12. $x = 0.17$.

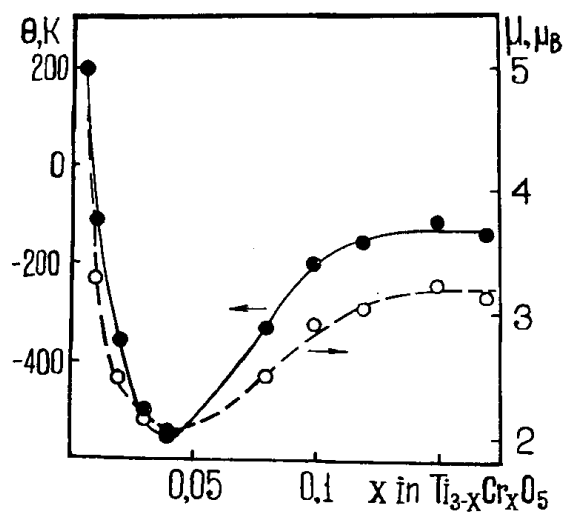


Fig. 5 Concentration dependences of magnetic moment per one ion of Cr in $\alpha\text{-Ti}_{3-x}\text{Cr}_x\text{O}_5$ ("a" model) and the Weiss constant ("b" model).

“a”. Assuming $\Theta = 0$ we take the model of “effective moments”. The concentration dependence obtained, μ_{eff} , is given in Fig. 5.

$$\mu_{\text{eff}} = \sqrt{\frac{8}{x}} C \quad (7)$$

where x - the amount of Cr-ions in formula unit $Ti_{3-x}Cr_xO_5$.

“b”. In this case the fixed values of Curie constants are calculated supposing that Cr^{3+} ions are the only kind of paramagnetic centres in the α -phase. $\Theta(x)$ dependence is given in Fig. 5.

The concentration dependences A , B , m and ε_0 obtained according to both models, are analogous. The monotonous increase of A and B is observed at increased Cr content in solid solutions, related with m^* increase. The growth of the electron effective mass indicates, in our opinion, the electron scattering on impurities, that is on Cr ions.

The dependence $\mu_{\text{eff}}(x)$ (model “a”) and $\Theta(x)$ (model “b”) shown in Fig. 5, represent characteristic curves with a minimum at $x = 0.04$. At $x = 0.12$ $\mu_{\text{eff}}(x)$ and $\Theta(x)$ become constant. Evidently, this dependence may be explained taking into account that the systems of collective and localized electrons interact. The exchange interaction of conductive and localized electrons may lead to indirect interaction of localized magnetic moments (RKKI-interaction). Sometimes this interaction may be of ferromagnetic nature [7]. The ferromagnetic interaction of Cr^{3+} and Ti^{3+} ions located in neighbouring sites, may explain the great value of the magnetic moment per Cr ion in the region of small concentrations. With the increasing Cr content in solid solutions the mean distances between impurity atoms are reduced and the possibility of direct antiferromagnetic interaction between Cr ions grows up. The sign change of Θ occurs and the magnetic moment decreases (Fig. 5). It should be mentioned that the similar concentration dependence μ is described in [8] for $(Ti_{1-x}V_x)_2O_3$. This result indicates it to be evidently regular for given type of compounds.

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