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Ferrimagnetic Properties of the $FeCr_2O_4$ Chromite and $TiFe_2O_4$ Titanomagnetite Minerals at High Temperatures

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Temperature dependence of the magnetic susceptibility of the $FeCr_2O_4$ chromite and $TiFe_2O_4$ titanomagnetite minerals in the temperature range 300–1300 K is studied. Based on the experimental dependences, the magnetic parameters of the samples are calculated: Curie temperature, Curie–Weiss constant C, effective magnetic moment per one magnetic ion of the compound, and magnetic moment per formula unit of the sample. The results obtained are analysed in the light of available theoretical models.

Key words: magnetic susceptibility, chromite, titanomagnetite, magnetic moment, paramagnetic Curie temperature, Curie–Weiss constant.

Досліджено температурну залежність магнетної сприйнятливости мінералів хроміту $FeCr_2O_4$ та титаномагнетиту $TiFe_2O_4$ в інтервалі температур 300–1300 К. За експериментальними залежностями обчислено магнетні параметри зразків: температуру Кюрі, сталу Кюрі–Вейсса C, ефективний магнетний момент, що припадає на один магнетний йон сполуки, та магнетний момент, що припадає на формульну одиницю зразка. Одержані результати проаналізовано в світлі наявних теоретичних моделів.

Ключові слова: магнетна сприйнятливість, хроміт, титаномагнетит, магнетний момент, парамагнетна температура Кюрі, стала Кюрі–Вейсса.

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1. INTRODUCTION

The fundamental difference between an iron-containing mineral and a rock is that the mineral, both in terms of its chemical composition and its physical properties, is a relatively homogeneous body, while rocks are aggregates of minerals consisting of a number of mineral components [1].

The physics of magnetism is able to predict the magnetic properties of materials from their structure; this also applies to rocks. However, this approach is not optimal: it requires an in-depth study of the structural characteristics of the substance, which is not available in geophysical research. On the other hand, measuring the magnetic properties of rocks is not difficult even with a large number of samples [2]. The nature of the magnetism of rocks and the characteristics of the factors that determine the patterns of distribution of the magnetic properties of various rocks must be supplemented with empirical data for the most common minerals of rocks and ores that cause magnetic anomalies [3, 4].

The magnetic states of rocks and ores are of particular interest for the physics of magnetic phenomena, since, due to the complex crystal structure, the magnetic structures of these minerals are necessary for understanding their key features [5]. There is little experimental data on the magnetic properties and electronic structure of rock minerals at high temperatures.

The study of the magnetic properties of rock minerals from the perspective of a mineralogist is extremely important. To date, the magnetic properties of these minerals have been studied mainly in their magnetically ordered state, while their paramagnetic state has been almost unstudied [6].

To date, the temperature dependence of the paramagnetic susceptibility $\chi(T)$ of pure iron has been measured in detail by many researchers [7–9] in a wide temperature range covering its liquid state and interpreted on the basis of the polymorphic and magnetic phase transitions occurring in iron. According to the results of these studies, the dependence $\chi^{-1}(T)$ of iron is complex. χ^{-1} grows abruptly at the temperature of the ferromagnet-paramagnet magnetic phase transition ($\Theta_p = 1043$ K); χ^{-1} increases linearly in the temperature range 1043–1183 K, and at the polymorphic transition α-Fe (b.c.c.)→γ-Fe (f.c.c.) (at 1183 K) decreases abruptly; in the temperature range 1183–1665 K, it increases linearly, and during the polymorphic transition γ-Fe (f.c.c.) →δ(α)-Fe (b.c.c.) (at 1665 K), it decreases abruptly; it increases in the temperature range 1665–1809 K linearly, during melting (1809 K) abruptly, and then linearly. By now, the magnetic properties of the compound of iron with non-magnetic metals at high temperatures have been little studied. This is due to the difficulty of making precision magnetic measurements at high temperatures.

The purpose of this work is to study experimentally the $\chi(T)$ dependence of the iron-containing minerals chromite and titanomagnetite included in the rocks of Uzbekistan. The dependences $\chi(T)$ were measured by the Faraday method using high-temperature vertical pendulum balances in Al_2O_3 crucibles and in an excess atmosphere of purified helium in the high temperature range 300–1300 K. The maximum relative measurement error for χ did not exceed 3% [8–11]. Rock (mineral) samples were obtained from the Central Research Laboratory of the Navoi Mining and Metallurgical Combine.

2. EXPERIMENTAL RESULTS AND DISCUSSION

The dependences $\chi(T)$ were measured in the temperature range 300–1200 K for chromite and 900–1300 K for titanomagnetite (Fig. 1).

Analysis of Fig.1 shows that, for the studied minerals of chromite and titanomagnetite, χ decreases with raising temperature, but the temperature dependence is complex [12].

The measurement results are shown in Fig. 2 in the form of $\chi^{-1}(T)$ dependence.

In Figure 2, it can be seen that the $\chi^{-1}(T)$ dependences of the minerals chromite and titanomagnetite in the studied temperature range have a nonlinear complex character: the slope $(d\chi^{-1}/dT)$ of the $\chi^{-1}(T)$ dependence for chromite at approximately 823 K sharply increases, and at 933 K, it decreases; for titanomagnetite at 1043 K, it sharply increases, and at 1173 K, it decreases. The $\chi^{-1}(T)$ dependence for chromite in the temperature ranges 300–823 K and 933–1173 K, and for titanomagnetite in the temperature ranges 923–1043 K and 1183–

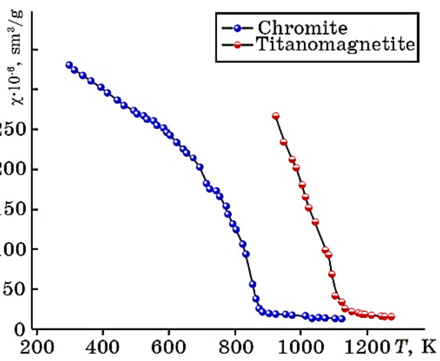

Fig.1. Dependences $\chi(T)$ of the studied samples of chromite $FeCr_2O_4$ and titanomagnetite $TiFe_2O_4$.

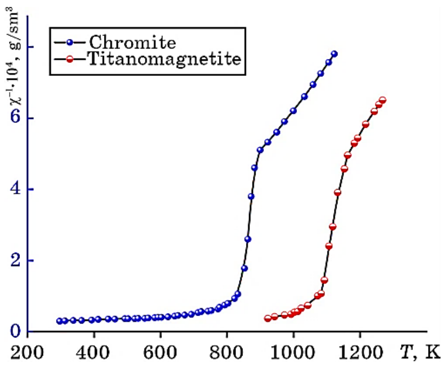

Fig.2. $\chi^{-1}(T)$ dependences of the studied chromite $FeCr_2O_4$ and titanomagnetite $TiFe_2O_4$ samples.

1273 K, they are linear.

The linear nature of $\chi^{-1}(T)$ dependence in the specified temperature range indicates that these dependences obey the Curie–Weiss law:

$$\chi = \frac{C}{T - \Theta_p}, \tag{1}$$

where C is the Curie–Weiss constant, Θ_p is the paramagnetic Curie temperature.

Changes in the experimental dependences $\chi^{-1}(T)$ of the samples under study can be explained by the results described above for pure iron [7, 8, 11]. The complex nature of $\chi^{-1}(T)$ dependence of pure iron is uniquely reflected in $\chi^{-1}(T)$ dependences of the studied iron-based compounds depending on temperature and the composition of non-magnetic elements (O).

Consequently, changes in the $\chi^{-1}(T)$ dependences of the studied samples occur due to magnetic and structural (polymorphic) phase transitions that occur in them at certain temperatures [13]. In chromite at 823 K, there is the structural transition f.c.c.→b.c.c. in its cubic lattice. In titanomagnetite at 1043 K, there is the structural transition f.c.c.→b.c.c. in its cubic lattice. These phase transitions are reflected in the $\chi^{-1}(T)$ dependence of chromite $FeCr_2O_4$ and titanomagnetite $TiFe_2O_4$ (Fig. 2) in the form of jumps at the temperatures of these transitions. Changes in the $\chi^{-1}(T)$ dependence in the studied minerals can only be explained by structural (polymorphic) transitions that occur at higher temperatures in Fe sublattices of these minerals [7,8].

From the experimental $\chi^{-1}(T)$ dependences for the studied samples, we calculated their main paramagnetic characteristics: Curie–Weiss constants C, paramagnetic Curie temperature Θ_p, and magnetic moment per mineral chemical formula μ_{for}. The calculation results are shown in Table. Information for pure iron in Table was obtained from [8]. Analysis of the table shows that the magnetic characteristics (Θ_p and μ_{for}) of the studied compounds are smaller compared to the magnetic characteristics of pure iron. This can be explained by an increase in the distance between the magnetic iron ions located at the sublattice sites of the studied compounds. Due to this reason, the magnetic exchange interaction of electrons in the 3d-shell of iron ions, which are responsible for the occurrence of magnetic ordering of the studied compounds, decreases. Θ_p is an energy measure of the exchange interaction.

Table shows that the values Θ_p for the studied minerals are lower compared to the values for pure iron ($\Theta_p = 1043$ K). This is explained by the fact that, if Fe^{3+} ions are partially or completely replaced by Cr^{3+} and Ti^{4+} ions in the crystal lattice of minerals, which in both structures show a strong tendency to occupy octahedral positions, this will lead to

TABLE. Calculation results.

Mineral	Temperature interval, K	Θ_p, K	C, 10^4 $sm^3 \cdot g^{-1} \cdot K$	μ_{for}, μ_B
Fe	1043–1183	1050	28,1	3.54
	1183–1665	–2027	90	6.47
	1665–1809	1100	25	3.34
Chromite $FeCr_2O_4$	300–820	60	1340	15.51
	930–1170	520	72.05	3.59
Titanomagnetite $TiFe_2O_4$	920–1040	850	250	7.48
	1180–1270	910	55.56	3.5

a significant decrease in the Curie temperature.

The distribution of cations between octahedral and tetrahedral positions in the titanomagnetite lattice has been the subject of extensive discussion [14]. According to neutron diffraction data, most of Ti^{4+} ions are located in octahedral positions. The spin moments of octahedral and tetrahedral ions are directed in opposite directions. As the number of Ti^{4+} ions increases, the Néel point decreases. Fe^{3+} prefers for octahedral sites, the actual distribution between octahedral and tetrahedral sites may depend on both temperature and composition.

4. CONCLUSIONS

Based on the results obtained, the following conclusions can be drawn. For the first time, the $\chi^{-1}(T)$ dependences of iron-containing minerals, chromite $FeCr_2O_4$ and titanomagnetite $TiFe_2O_4$, were measured at high temperatures. It has been established that these $\chi^{-1}(T)$ dependencies obey the linear Curie–Weiss law.

Based on the experimental dependences of the studied minerals, their main paramagnetic characteristics were determined.

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