

Magnetic susceptibilities of chromites from Oman

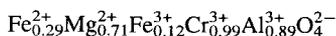
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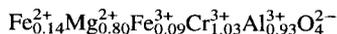
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MINERALOGICAL and physical characteristics of natural chromites from Oman ophiolites have been recently investigated using Mössbauer spectroscopy (MS), X-ray diffraction (XRD) and Scanning electron microscopy (SEM) by Al-Alawi *et al.* (1996). From the MS analysis together with the SEM data, they derived the chemical formula for specimens collected from two separate chromite deposits named Tawiyah (15 km NNW of Nakhal) and Khobar (on the Luzugh-Semail road) and proposed respectively as follows:



and



Furthermore, their MS data reveal that the ferrous/ferric ratio remains constant at different temperatures which suggests an ordered distribution of the cations. The aims of this work are to characterize further the specimens of natural chromite from Tawiyah and Khobar and to investigate their magnetic properties taking into account the results of the earlier study.

First, the raw powdered samples were sieved to eliminate the fine fraction and retain grains with size larger than 335 μm . Then they were passed through a magnetic separator in order to remove the gangue from the pure chromite. Finally, they were examined under the binocular microscope up to 100 \times magnification showing the dark chromite grains and the remaining clear gangue grains. This separation process was repeated as often as necessary until no observable impurities remained. The X-ray measurements revealed that some traces of Ti and Mn (< 0.01%) were present but have been neglected in establishing the chemical formulae.

The magnetic susceptibility measurements were performed using a Faraday analytical microbalance of 1 μg precision. An electromagnet with specially shaped poles for constant field gradient, produced field strengths of 4, 5 and 6 kOe. The magnet was calibrated with Mohr's salt having a susceptibility of $32.32 \times 10^{-6} \text{ emu g}^{-1}$ at 20°C. During the experiment, the sample was contained in a quartz bucket having a temperature independent diamagnetism over a wide range which could be subtracted from the measured magnetic force. An Oxford liquid nitrogen cryostat provided with a heater enabled scanning the temperatures between 77 and 500 K.

The data of the mass magnetic susceptibility χ_m inverse versus temperature T are shown in Fig. 1. As can be seen, the Khobar specimen data are magnetic field dependent especially in the middle range, most probably because of some remaining magnetic impurities. In order to extract the purely paramagnetic contribution, we then had to extrapolate to infinite field ($1/H \rightarrow 0$) as shown in the figure. The Tawiyah specimen data are field independent. The order of magnitudes of χ_m confirms well the paramagnetism detected by the MS spectra of Al-Alawi *et al.* (1996) for both specimens down to 77 K. However, it is difficult to determine the magnetic transition temperature by extrapolation since our lowest point is certainly above the known measured Néel temperature of 75 K (Murad and Johnston, 1987).

In Fig. 1, the curves of both specimens present a bending at approximately 160 K. This singularity can also be seen more clearly in the first derivative of χ_m versus T . This has been obtained by first smoothing the data using the cubic splines technique then by analytical derivation. The results of $d\chi_m/dT$ against T

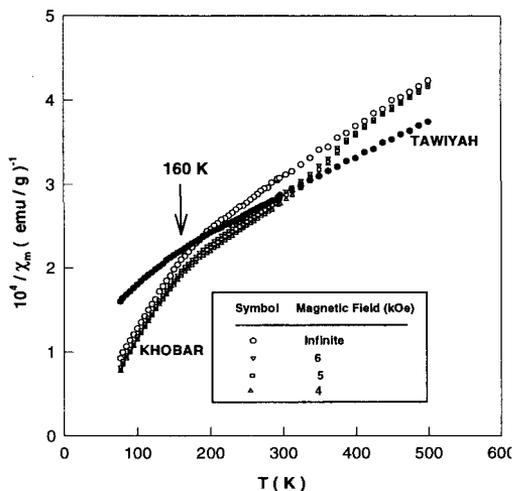


FIG. 1. Inverse of mass magnetic susceptibility vs. temperature of natural chromite from Oman

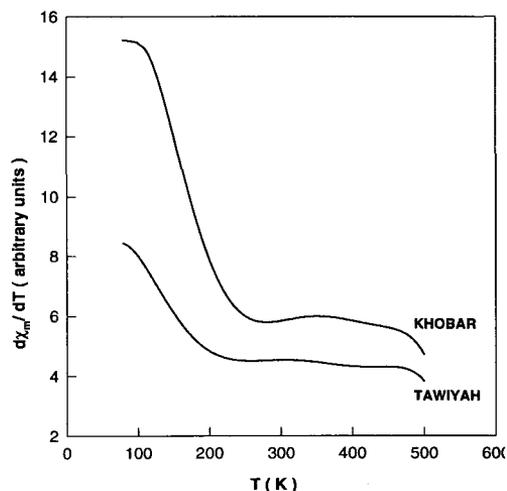


FIG. 2. Derivative of mass magnetic susceptibility vs. temperature of natural chromite from Oman.

are shown in Fig. 2. Indeed, both specimens show a sharp drop around 160 K then a flat region at high temperature.

These anomalies are not unique, but somewhat similar trends have been observed by Lodya *et al.* (1994) in natural chromite from the Bushveld Complex in South Africa. They suggested that this is due to a structural phase transition which they found evident from the broadening of the Mössbauer linewidth at approximately the same temperature (Lodya *et al.*, 1994; Mitra *et al.*, 1991; Fatseas *et al.*, 1976). Indeed, our specimens did show a broadening of the Mössbauer spectrum between 77 and 298 K (Al-Alawi *et al.*, 1996), but whether this starts occurring at 160 K requires a more scrupulous investigation.

On the basis of such structural phase transition, we are inevitably led to look at the change in the effective magnetic moments for both specimens at the point where the singularity occurs. These can be extracted by considering a Curie-Weiss model of the mass susceptibility of the form:

$$\frac{1}{\chi_m} = \frac{M}{C} (T - \theta)$$

Where C is the Curie constant, θ is the Weiss constant and M the molar mass of the specimen. The effective magnetic moment μ_{eff} per molecular formula unit is related to C by:

$$\mu_{\text{eff}} = 2.84\sqrt{C} \quad \text{in Bohr magneton units}$$

This has been fitted separately to either side of 160 K. The results are shown in Table 1.

The values of Tawiyah are higher than those of Khobar which is consistent with the higher stoichiometry of Fe^{2+} and Fe^{3+} and approximately the same stoichiometry of Cr^{3+} as the chemical formulae show. Furthermore, if we consider the high spin state values of Fe^{2+} , Fe^{3+} and Cr^{3+} as 4.9, 5.92 and $3.87 \mu_B$ respectively, and assume an additivity given the chemical formulae, the calculated magnetic moments per mole are 3.1 and $3.9 \mu_B$ for Tawiyah and Khobar respectively. Again, this increase is

TABLE 1. Effective magnetic moments μ_{eff} and Weiss constant θ above and below 160 K

Specimens	Khobar		Tawiyah	
	> 160 K	< 160 K	> 160 K	< 160 K
$\mu_{\text{eff}} (\mu_B)$	4.8	3.3	5.7	4.6
θ (K)	-240	+10	-260	-120

consistent with our experimental results at least qualitatively. We may add that smaller observed magnetic moments than the theoretical quenched values are not uncommon when ionic type of bonding is involved since crystal field effects are subject to complex variations (Robins *et al.*, 1971). As far as the ordered distribution of the cations is concerned, as concluded by Al-Alawi *et al.* (1996), this is difficult to correlate with the structural phase transition and the change in the paramagnetic moments.

Acknowledgements

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Morimotoite, a new titanian garnet? — discussion

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THE valence state and site distribution of titanium in andradite remains a matter of much discussion. In a recent paper, Henmi *et al.* (1995) described a new mineral morimotoite, $\text{Ca}_3\text{TiFe}^{2+}\text{Si}_3\text{O}_{12}$, found in contaminated rocks at Fuka, Bitchu-Cho, Okayama Prefecture, Japan. The morimotoite chemical composition (mean of seven microprobe analyses) and its cell dimensions are presented in Table 1, together with an earlier known titanian andradite (schorlomite

from nepheline syenite, Iivaara, Finland, Deer *et al.*, 1982. N24 after Zedlitz, 1935) shown for comparison.

Apparently, both analyses are closely similar. Note that the wet-chemical analysis from Zedlitz (1935) contains no Fe^{2+} , whereas the analysis of morimotoite includes Fe^{3+} and Fe^{2+} , calculated on the basis of 8 cations per 12 oxygens. Hence, the latter mineral may be either the first find at Fuka or in these rocks,