Journal of Research in Physics Vol. 29, No. 1, 79 - 83 (2002)

Magnetic Properties of Cr(III) and Fe(III) Ions in Hexaaqua-Nitrate-Trihydrates

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Received: *September 24, 2001*

Abstract

The manuscript contains new measurements and calculations of magnetic susceptibility of Cr(III) and Fe(III) ions in hexaaqua-nitrate-trihydrate. The magnetic properties of the ion M=Cr(III), Fe(III) in hexaaqua-nitrate-trihydrate $M(H_2O)_6(NO_3)_3{\cdot}3H_2O$ were studied from the temperature dependence of magnetic susceptibility determined using the SQUID susceptometer, within the temperature range $4\ K \leq T \leq 290\ K$. The detected deviation from the Curie-Weiss law is explained by the splitting of the ground state energies of the magnetic ions under the influence of the crystalline field (splitting in the zero field) and the contribution of the temperature independent Van-Vleck paramagnetism.

Key words: Magnetic susceptibility, Cr(III) and Fe(III) ions, crystalline field

1. Introduction

It is known that magnetic ions in crystals are exposed to the influence of the crystal surrounding (named "ligand" or "crystalline" field). The crystalline field can change the magnetic properties of ions in relation to free ion properties. The systems, which contain isolated magnetic ions, are close to an ideal paramagnetic substances and they are very convenient for research of the crystalline field effect. The absence of magnetic interaction between ions, gives an opportunity to observe only the crystalline field effect. The hexaaqua-nitrate-trihydrate $M(H_2O)_6(NO_3)_3{\cdot}3H_2O$, M=Cr(III), Fe(III), which is the object of this research is a very good example of such systems.

The single crystals of Cr(III) and Fe(III) hexaaqua-nitrate-trihydrates were obtained by slow crystallization from a saturated aqueous solution of pure compounds $Cr(NO_3)_3{\cdot}9H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$. The crystal structures of Cr(III) and Fe(III) hexaaqua-nitrate- trihydrates were solved using a single crystal X-ray diffraction method. It was confirmed that the samples are isostructural. These materials crystallize in monoclinic system, space group $P2_{1/c}$ (No 14) [1,2]. Cations Cr(III) and Fe(III) occupy two distinct unequivalent special positions [(a) 0,0,0; 0,0.5,0.5; (d) 0.5,0.5,0.5; 0.5,0.5,0] local symmetry $\bar{1}$. Coordinated polyhedra of cations are distorted octahedra. The distortion can be considered as an axial symmetric and equal for both special positions. The electron structure of $Cr(NO_3)_3{\cdot}9H_2O$ was analyzed using diffusion-reflection and UV spectra of powder sample [3].

It is known that the free ion Cr(III) ground state is ^{4}F ($S = 3/2$, $L = 3$). The regular octahedra crystalline field splits this state into three orbital multiplets. The ground level is orbital singlet $^4A_2(g)$ with spin $S = 3/2$ (Figure 1(a)). Because of axial distortion of the octahedral surrounding, this ground state splits (zero field effect) into two doublets $S = \pm 3/2$, $S = \pm 1/2$ [4]. The energy level distance between these doublets is D (Figure 1(a)). The energy level distances between ground multiplet and excited multiplets $^4T_2(g)$ and $^4T_1(g)$ are approximately 17000 cm^{-1} and 24000 cm^{-1}, respectively [3].

The free ion Fe(III) ground state is an orbital singlet ^{6}S ($S = 5/2$, $L = 0$). The regular octahedral crystalline field does not split the ground state of free Fe(III) ion. The distorted octahedral surrounding (zero field effect) splits this ground state into three doublets with energy level distances D_1 and D_2, as shown in Figure 1(b). The energy level distances formed by zero field effect could be determined using magnetic measurements.

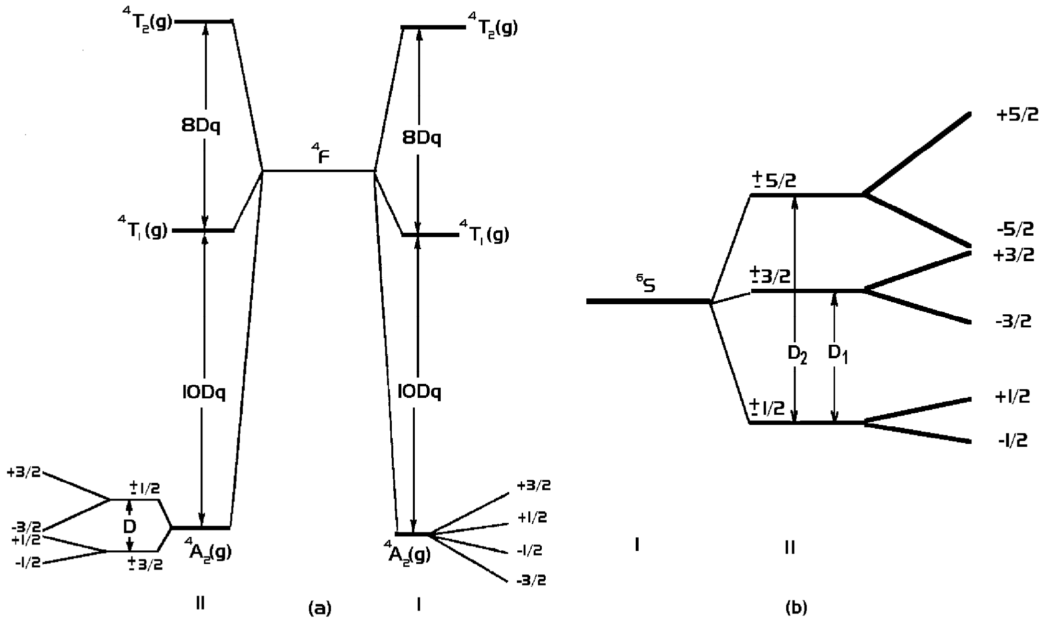

Figure 1. Orbital singlet splitting in regular (I) and distorted (II) crystalline field for: (a) Cr(III) ion, (b) Fe(III) ion.

Generally, the magnetic susceptibility of isolated ions in the crystalline field could be described by Van-Vleck equation [4]:

$$\chi = \frac{N \sum_n [(E_n^{(1)})^2/kT - 2E_n^{(2)}] \exp\{-E_n^0/kT\}}{\sum_n \exp\{-E_n^0/kT\}} \tag{1}$$

In the previous equation, the energy level is developed into a series in terms of the applied magnetic field - H: $E_n = E_n^0 + HE_n^{(1)} + H^2E_n^{(2)}$

2. Results and discussion

We wanted to connect the physical properties of Cr(II) and Fe(III) hexaaqua-nitrate-trihydrates with the known crystal structure. For this purpose, we additionally performed magnetic measurements. The temperature dependence of the magnetic susceptibility of the examined materials was determined using the SQUID susceptometer, within the temperature range 4 K$\leq T \leq$ 290 K in magnetic field 1T. The experimental data of the inverse magnetic susceptibility, per gram-ion are shown in Figures 2 and 3. We concluded that both samples are in paramagnetic phase in a whole measurement temperature range. It can be clearly seen that the experimental data show deviation from the Curie-Weiss law, so we can describe the experimental data with Van-Vleck equation (1) applied to 3d ions in crystalline field, with energy spectra as it is shown in Figures 1(a) and 1(b).

In both cases of ions Cr(III) and Fe(III) we can ignore the excited level population due to the great energy splitting. The only levels, which are populated, are formed from the ground state splitting in the crystalline field. The influence of excited multiplets, are taken into consideration only as the temperature independent Van-Vleck contribution (second order Zeeman effect) χ_{TIP} , in case of Cr(III) ions. In the case of Fe(III) ions, there is no ground state splitting in the regular crystalline field, so we can ignore the temperature independent Van-Vleck paramagnetism. Taking into account the above explained, as well as the fact that the zero field effect exists in case of both ions, Van-Vleck equation obtain forms:

$$\chi = \frac{Ng^2\mu_B^2}{4kT}\left[\frac{1+9\exp\{-D/kT\}}{1+\exp\{-D/kT\}}\right] + \chi_{TIP} \tag{2}$$

$$\chi = \frac{Ng^2\mu_B^2}{4kT}\left[\frac{1+9\exp\{-D_1/kT\}+25\exp\{-D_2/kT\}}{1+\exp\{-D_1/kT\}+\exp\{-D_2/kT\}}\right] \tag{3}$$

for Cr(III) and Fe(III) ions, respectively.

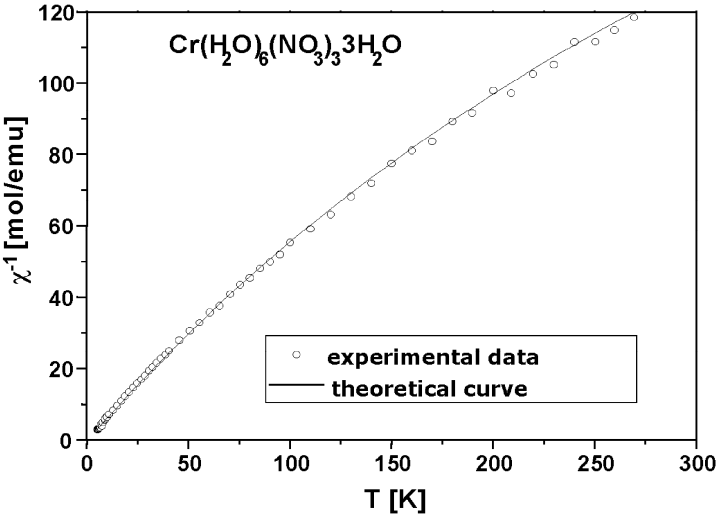

Figure 2. Inverse magnetic susceptibility for Cr(III) ions in hexaaqua-nitrate-trihydrate. Theoretical curve is obtained using equation 2 for fitting experimental data.

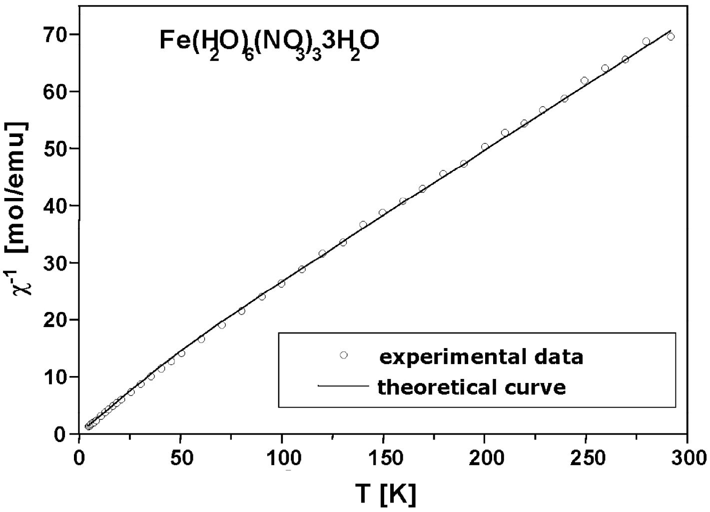

Figure 3. Inverse magnetic susceptibility for Fe(III) ions in hexaaqua-nitrate-trihydrate. Theoretical curve is obtained using equation 3 for fitting experimental data.

The experimental data for Cr(III) and Fe(III) ions in hexaaqua-nitrate-trihydrates were fitted using expressions (2) and (3) respectively. In the case of Cr(III) ions, the fitted parameters were energy level distance D, temperature independent Van-Vleck paramagnetism χ_{TIP} and Lande splitting factor g. Including the Lande splitting factor as the fitted parameter, we considered the contribution of spin-orbit interaction as a result of orbital momentum incomplete freezing. The fitted parameters in the case of Fe(III) ions were energy level distances D_1 and D_2. In this case, we treated the Lande splitting factor as constant value. The calculated values of inverse susceptibility are shown in Figures 2 and 3. Calculated values of fitted parameters are given in Table 1.

Table 1. Calculated values of fitted parameters.

ion	calculated values of fitted parameters
Cr(III)	$D = (1.6 \pm 0.2)\ \mathrm{cm}^{-1}$; $g = 1.9 \pm 0.05$; $\chi_{TIP} = (8 \pm 2) \cdot 10^{-4}$ emu/mol
Fe(III)	$D_1 = (80 \pm 3)\ \mathrm{cm}^{-1}$; $D_2 = (12 \pm 1)\ \mathrm{cm}^{-1}$

3. Conclusion

We performed the measurements of the temperature dependence of the magnetic susceptibility of Cr(III) and Fe(III) hexaaqua-nitrate-trihydtates samples. The results of the measurements show that the samples are in a paramagnetic phase in whole measurement temperature range. The results also show deviation from the Curie-Weiss law. On the basis of identified crystal and electron structure, we calculated zero field splitting parameters in the case of both ions. In the case of Cr(III) ions, we calculated the temperature independent Van-Vleck contribution and the Lande splitting factor value.

The calculated value D for the Cr(III) ion is close to the values from literature [5]. The level with $S = \pm 1/2$ is the lowest in energy level arrangement, inverse from Figure 1(a).

The calculated Lande splitting factor value differs slightly from spin only value. This fact shows a partial orbital momentum "unfreezing" as a result of spin-orbital coupling. The calculated value for χ_{TIP} agrees with literature data [6].

The level with $S = \pm 3/2$ is the lowest in the energy level arrangement of Fe(III) ion, the level with $S = \pm 1/2$ comes next.

Obtained results show that the used model of axial distorted crystalline field is a good approximation for observed materials. It should also be mentioned that the energy level splitting is more frequently determined by spectroscopic methods, since magnetic measurements are unsatisfactorily sensitive.

Acknowledgments

This work was supported by a research grant No.2022-OI: "Physical Properties of Bulk and Nanoparticled Rare Earths and Transition Metal Based Magnetic Materials" from the Ministry of Science, Technologies and Development of the Republic of Serbia.

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