# MAGNETIC BEHAVIOUR OF IMPERFECT QUASI ONE DIMENSIONAL INSULATORS FeMgBO4 AND FeMg2BO5 : SPIN GLASS SYSTEMS ?

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# MAGNETIC BEHAVIOUR OF IMPERFECT QUASI ONE DIMENSIONAL INSULATORS $FeMgBO_4$ AND $FeMg_2BO_5$ : SPIN GLASS SYSTEMS ? †

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*Centre d'Etudes Nucléaires, 85 X, 38041 Grenoble Cedex, France*

Résumé.- Les mesures de susceptibilité, chaleur spécifique, effet Mössbauer et diffraction neutronique réalisées sur les composés isolants quasi unidimensionnel $FeMgBO_4$ et $FeMg_2BO_5$ ont mis en évidence des propriétés magnétiques du type verre de spin dues à des effets d'impureté résultant d'une inversion de 10 % des ions $Fe^{3+}$ et $Mg^{2+}$.

Abstract.- The measurements of susceptibility, specific heat, Mössbauer effect and neutron diffraction performed on the quasi one-dimensional insulators $FeMgBO_4$ and $FeMg_2BO_5$ have shown a magnetic behaviour of the spin glass type due to impurity effect resulting of a 10 % site inversion of $Fe^{3+}$ and $Mg^{2+}$.

INTRODUCTION.- The investigation of low dimensional magnetic systems and spin glasses have received much interest in the last ten years. The "BOROFERRITES" $FeMgBO_4$ and $FeMg_2BO_5$ are insulators of orthorhombic structure /1,2/. In $FeMgBO_4$ $Fe^{3+}$ ions (in the centers of oxygen octahedron) form zig-zag chains in the c-direction with distances of 2.6 Å between nearest neighbours and 3 Å between next nearest neighbours, this equal to the Fe-Fe distance within the linear chains built up in $FeMg_2BO_5$. In both compounds magnetic chains are separated by linear chains of diamagnetic $Mg^{2+}$ ions and $B^{3+}$ ions at a distance of 6 Å. From this arrangement isotropic quasi 1D exchange interaction between the nearest and next nearest $Fe^{3+}$ ions (S = 5/2) in $FeMgBO_4$ and between only nearest neighbours in $FeMg_2BO_5$ should be attended. This paper summarizes the results of an investigation on magnetic behaviour of these compounds.

EXPERIMENTAL RESULTS.- Well crystallized samples were prepared by melting stoechiometric quantities of $Fe_2O_3$, $B_2O_3$ and MgO in dehydrated borax at 950°C and 1120°C for $FeMgBO_4$ and $FeMg_2BO_5$ respectively, followed by slow cooling.

Susceptibility measurements on powdered samples in the temperature range 1.8 - 300 K show that both compounds follow a Curie-Weiss law above 150 K (figure 1) with effective moments $\mu_{eff}$ close to the spin only value for S = 5/2. From the large negative values of the paramagnetic Curie temperature θ, indicating strong antiferromagnetic coupling, we deduced the exchange integrals by means of the MF-prediction θ = 2zJS(S+1) / 3 K (table I).

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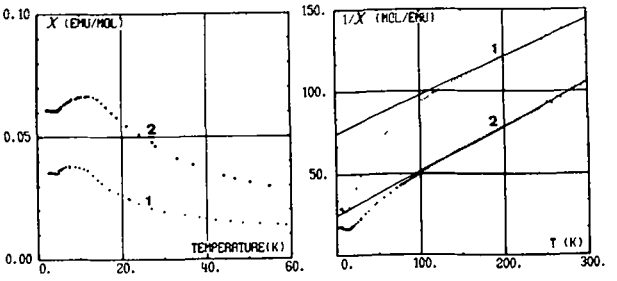


Fig. 1 : Magnetic susceptibilities and their inverse of $FeMgBo_4$ (curves 1) and $FeMg_2BO_5$ (curves 2) corrected by ion-diamagnetism, measured in a field of H = 1555 Oe. The full lines in the right hand part represents the Curie-Weiss law for T = 150 K.

Table I

Results of susceptibility measurements

| | C (emu/mol K) | $\mu_{eff}$ ($\mu_B$) | θ (K) | $T_{max}$ (K) | $T_{max}/\theta$ | J/K |
|---|---|---|---|---|---|---|
| $FeMgBO_4$ | 3.958 | 5.65 | -286 | 7.0 | 0.024 | -24 |
| $FeMg_2BO_5$ | 3.833 | 5.56 | -100 | 11.8 | 0.118 | - 8 |

Below 150 K the susceptibilities increase more rapidly than a Curie-Weiss law and pass through a maximum at $T_{max}$ (figure 1) which is shifted to lower temperatures when the applied field is increased. Below $T_{max}$ a small hysteresis effect together with

a small thermoremanent magnetization (TRM) is observed when the sample is cooled in strong external fields through $T_{max}$. Magnetization measurements on a single crystal did not show evidence of a deviation of the parallel and perpendicular susceptibilities.

Mössbauer spectra of $FeMgBO_4$ and $FeMg_2BO_5$ above temperatures $T_{max}$=10 K and 16 L respectively consist of a single symmetric quadrupole-split doublet with parameters of isomer shift (IS) and quadrupole-splitting (QS) typical for high-spin $Fe^{3+}$ ions in octahedral sites. Below $T_M$ the doublet disappears completely and a magnetic hyperfine splitting occurs The lines of the sextette are rather broas even at 1.2 K indicating superposition of different hyperfine fields. The average value is 436 kOe in $FeMgBO_4$ and 470 kOe in $FeMg_2BO_5$, these values are smaller than expected for $Fe^{3+}$ ions.

Neutron diffraction experiments, performed on powdered samples enriched with $^{11}B$ did not show evidence of tridimensional magnetic ordering down to 0.7 K however an evolution of the diffuse background at low scattering angles indicates the presence of short range order effects. The analysis of the nuclear Bragg peak intensities taking into account the degree of inversion x between $Fe^{3+}$ and $Mg^{2+}$ ions $(Fe_{1-x}Mg_x)(Fe_xMg_{1-x})Bo_4$, leads to x = 0.1 with reliable factor R = 0.02. Particularly the intensities of the well separated peaks 110, 210, 111, 400 whose structure factors are very sensitive to inversion, agree only with x = 0.1.

Specific heat measurements were carried out in the temperature range 1.2 K - 60 K on $FeMgBO_4$ and $GaMgBO_4$ as a diamagnetic isomorphous which show the contribution of phonons to the specific heat (figure 2). By substracting $C(GaMgBO_4)$ from the total specific heat of $FeMgBO_4$ we obtained the thermal variation of the magnetic specific heat (figure 2b) which shows a maximum near 45 K but not λ-type anomaly. Between 3 K and 14 K the best fit of data was obtained by a linear temperature function :

$$C_{magn.} = -151.6 + 146\ T\ (mJ/molK)$$

with a negative value of the T-independent term, indicating a partial freezing of degrees of freedom. Below 3 K C(T) was fitted by a polynom with a dominating linear term :

$$C_{magn.} = 47.4\ T + 10.8\ T^2 + 1.83\ T^3\ (mg/molK)$$

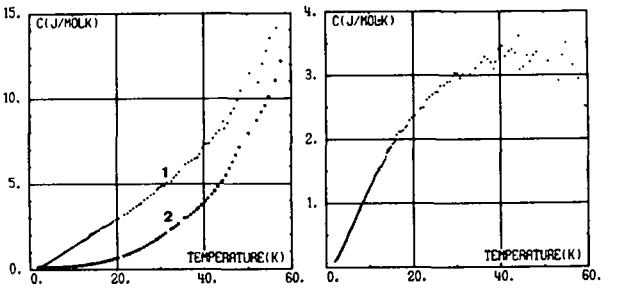


Fig. 2 : a) molar specific heat of $FeMgBO_4$ (1) and of its diamagnetic isomorphous $GaMgBO_4$ (2)
b) thermal variation of the magnetic part of specific heat of $FeMgBO_4$ :
$C_{magn.} = C_{FeMgBO_4} - C_{GaMgBO_4}$

DISCUSSION.- The large value of J(J/k = 24 K) in $FeMgBo_4$ can be explained as the sum of two exchange constants $J_1$ and $J_2$ describing nearest and next nearest neighbours interactions respectively within the zig-zag chain. $J_2$ will be equal to the single exchange integral of $FeMg_2BO_5$ (J/k = -8 K) since the Fe-Fe distance within the linear chain is the same as between next nearest neighbours in $FeMgBO_4$ and we find the reasonable value of nearest neighbours interactions $J_1/k = -16$ K. The competition between the two intrachain interactions with a ration $J_1/J_2 = 2$ should then lead to a helical ground state in the quasi one dimensional system $FeMgBO_4$ /3,4/ since $FeMg_2BO_5$ should be an example of 1D-Heisenberg antiferromagnet with only nearest neighbour interaction. In fact the low temperature results of susceptibility and magnetization measurements are not in agreement with theoretical predictions of such pure systems. Positive deviation of χ from the Curie-Weiss law and the appearence of TRM can be explained by formation of clusters with partially uncompensated spins as a consequence of the 10 % site-inversion : $Mg^{2+}$ as diamagnetic impurity cut the magnetic chains in $FeMg_2BO_5$ whereas in $FeMgBO_4$ only the coupling between one pair of nearest neighbours but not between the next nearest neighbours is suppressed by $Mg^{2+}$. The Mössbauer sextette below $T_M$ indicate that these chain-segments are coupled as well by the interchain interaction J' as by coupling through the $Fe^{3+}$ on the Mg sites between the chains. The competition of such different interactions can lead to a spin glass like behaviour so that no tridimensional long range order will be observed in neutron diffraction experiments. Several authors have considered theoretically the problem of impurities in

1-D systems and have concluded that spin glass behaviour is possible /5,6/.

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