ELECTRONIC AND MAGNETIC PROPERTIES OF FeBr$_2$

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Electronic and magnetic (e-m) properties of FeBr$_2$ have been surprisingly well described as originating from the Fe$^{2+}$ ions and their fine electronic structure. The fine electronic structure have been evaluated taking into account the spin-orbit (s-o) coupling, crystal-field and inter-site spin-dependent interactions. The required magnetic doublet ground state with an excited singlet at D=2.8 meV results from the trigonal distortion. This effect of the trigonal distortion and a large magnetic moment of iron, of 4.4$\mu_B$, can be theoretically derived provided the s-o coupling is correctly taking into account. The obtained good agreement with experimental data indicates on extremaly strong correlations of the six 3d electrons in the Fe$^{2+}$ ion yielding their full localization and the insulating state. These calculations show that for the meaningful analysis of e-m properties of FeBr$_2$ the spin-orbit coupling is essentially important and that the orbital moment (0.74 $\mu_B$) is largely unquenched (by the off-cubic trigonal distortion in the presence of the spin-orbit coupling).
I. INTRODUCTION

FeBr$_2$ became famous long time ago as one of the strongest metamagnet [1,2]. At 4.2 K an external field of 3.15 T causes a jump of the magnetization from the almost zero value to a very big value of 110 emu/g [1,2]. This latter value corresponds to 4.4$\mu_B$ per formula unit (f.u.). Attributing this magnetization to the iron ions only one comes to the same value for one Fe atom. As this value exceeds a theoretical value of 4.0$\mu_B$, expecting for the spin-only moment, explanation for the origin of this large magnetic moment is a challenge for the 3d-magnetism theoreticians. FeBr$_2$ exhibits the antiferromagnetic ordering below $T_N$ of 14.2 K. The appearance of the AF ordering is marked in the specific heat as very pronounced $\lambda$-type of peak [3,4]. The appearance of the AF state is also seen in the temperature dependence of the magnetic susceptibility [5,6]. Properties of FeBr$_2$ have been tried to be described using effective Hamiltonians like the $S_{eff}=1/2$ Ising Hamiltonian [7] or $S_{eff}=1$ model with the anisotropic exchange [7,8]. Although those Hamiltonians had the intention to describe properties of the Fe$^{2+}$ ion such the effective description with fictitious $S=1/2$ or $S=1$ is largely invalid owing to the fact that the Hund’s rules give for the Fe$^{2+}$ ion the real spin quantum number $S=2$ [9,10]. Moreover, the neglect of the orbital contribution, due to the so-called quenching of the orbital moment, in these effective approaches to the 3d-magnetic ions is not any more justified. Thus we have performed exact calculations of the Fe$^{2+}$-ion electronic structure taking into account the spin and orbital electronic phenomena. In fact, we have used the well-known Hamiltonian for the 3d ion

$$H_d = H_{CF} + H_{s-o} + H_{ex}$$

**but we have performed exact quasi-atomic calculations in the $|LSLzS_z\rangle$ basis.**

In this paper we present results of calculations of electronic and magnetic (e-m) properties of FeBr$_2$ with the aim of providing the consistent physical description of zero-temperature properties (e.g. the magnetic-moment value and its direction, the insulating state) as well as temperature dependence of the specific heat and the paramagnetic susceptibility. It turns
out that e-m properties of FeBr$_2$ are predominantly determined by the low-energy electronic structure of the Fe$^{2+}$ ions. The Fe$^{2+}$ ion is considered to form the 3$d^6$ system described by S=2 and L=2. The low-energy electronic structure results from the removal of the 25-fold degeneracy. It turns out that there are 15 localized states within 80 meV, 10 others lying more than 2 eV above. The existence of this fine electronic structure causes strong thermal effects in the temperature course of the specific heat and the magnetic susceptibility. In fact, we have performed quite similar calculations to those that have been successfully made for description of rare-earth systems like ErNi$_5$ [11] or NpGa$_2$ [12]. Of course, the electronic states of the 3$d$ ion are calculated in the completely different way owing to much smaller spin-orbit coupling in 3$d$ ions.

II. THEORETICAL OUTLINE

A. The individualized-electron model analysis

The model applied to ErNi$_5$ or NpGa$_2$ can be called an individualized-electron model in analogy to the band(itinerant)-electron and localized-electron model. By this name it is pointed out that atoms in the solid preserve much of their atomic individual properties and we have to analyze individual electronic states. For FeBr$_2$ the starting analysis of experimental data within the individualized-electron model can be performed as follows:

1. from the insulating state of FeBr$_2$ we infer the electronic configuration Fe$^{2+}$Br$_2$$^{1-}$;
2. the opposite ionic charges assure the global stability of the compound due to the conventional Coulomb interactions;
3. the Br$^{1-}$ ion is electronically, below 3-4 eV, and magnetically silent as having all full electronic shells of $^{36}$Kr; the $^{36}$Kr-like shell shows weak diamagnetism with the negligibly small value of 5·10$^{-5}$µ$_B$/T,
4. thus, the low-energy electronic structure and the magnetism of FeBr$_2$ is attributed to the single-ion Fe$^{2+}$ states.
5. FeBr$_2$ has a yellow colour - it points to the existence of an energy separation of 2.0-2.2 eV;

6. FeBr$_2$ exhibits the antiferromagnetic order below $T_N$ of 14.2 K,

7. from the crystallographic structure it is known that the Fe ion in FeBr$_2$ is surrounded by 6 Br ions [4,6,8]; the Br ions form the almost cubic octahedral surrounding (this fact can be somehow surprising owing to the hexagonal elementary cell);

8. from detailed crystallographic considerations we note that this octahedral surrounding in the hexagonal unit cell can be easily distorted along the local cube diagonal; in the hexagonal unit cell this local cube diagonal lies along the hexagonal c axis and the related distortion can be described as the trigonal distortion.

B. The Fe$^{2+}$ ion

The Fe$^{2+}$ ion has 6 3$d$ electrons. In our approach they form the highly-correlated $d^6$ electronic system fulfilling the Russel-Saunders LS-coupling scheme with the ground term described by Hund’s rules. Such the approach is different from the present band structure theories that consider, at least at the start, these 6 electrons as largely independent (the one-electron approach) introducing later (strong) electron correlations. Thus our treatment starts from the opposite limit, i.e. from the highly-correlated electrons within the incomplete 3$d$ shell. The comparison with experiments should verify these approaches. Results of our calculations indicate the significant physical adequacy of our approach.

C. The electronic structure of the Fe$^{2+}$ ion as the highly correlated 3$d^6$ system.

The 3$d^6$ system, according to Hund’s rules, is described by S=2 and L=2 and the ground term is $^5$D. This term is 25-fold degenerated (see ref. [13], for instance). The 25-fold degeneracy is removed by:

1. the cubic crystal-field, ($H_{cub}^{CF}$)
2. the spin-orbit coupling ($H_{s-o} = \lambda L \cdot S$)
3. the trigonal-lattice distortion (\(B^0_2O^0_2\)).

These interactions have been written in the decreasing energy sequence.

The 25 levels and their eigenfunctions have been calculated by the direct diagonalization of the Hamiltonian (1) within the \(|LSL_zS_z\rangle\) base. It takes a form [14]:

\[
H_d = H_{\text{cub}} + \lambda L \cdot S + B^2_0O^2_0 + \mu_B(L + g_sS) \cdot B_{\text{mol}}
\]  

(2)

The separation of the crystal-electric-field (CEF) Hamiltonian for the cubic and off-cubic part is made for the illustration reason as the cubic crystal field is usually very predominant. The obtained energy level scheme is shown in Fig. 1.

The cubic CEF Hamiltonian takes, for the z axis along the cube diagonal, the form

\[
H_{\text{cub}} = -\frac{2}{3}B_4 \cdot (O^0_4 + 20\sqrt{2}O^2_4)
\]  

(3)

\(O^m_n\) are the Stevens operators. These three above-mentioned interactions yield a magnetic doublet ground state with an excited singlet at 33 K, see Fig.1e. The degeneracy of the ground doublet is spontaneously removed by the formation of the magnetic order. Then in calculations a Zeeman-like Hamiltonian

\[
H_z = -\mu_B(L + g_sS) \cdot B_{\text{mol}}
\]  

(4)

with \(g_s=2.0023\) and the molecular field \(B_{\text{mol}}\) appears.

**D. The inter-site spin interactions in FeBr\(_2\)**

In the ordered state occurring below 14.2 K the molecular field is set up self-consistently as \(B_{\text{mol}} = -n < m_d >\), where \(n\) is the molecular-field coefficient and \(m_d = -\mu_B(L + g_sS)\). It originates from inter-site spin interactions. Thus our full Hamiltonian for FeBr\(_2\) contains two, intra- and inter-ion, terms:

\[
H = \sum H_d + \sum H_{d-d}
\]  

(5)
where summation goes over all d ions. \( H_{d-d} \) originates from the Zeeman-like term and is written as

\[
H_{d-d} = \sum \sum n \cdot (m_d \cdot < m_d > - \frac{1}{2} < m_d >^2)
\]

(6)

The last term in (6) is included in order to avoid the double counting (see, for instance refs 11,12). The summation goes over all pairs of magnetic ions. This inter-site interactions produce the magnetic state; in case of FeBr\(_2\) it is antiferromagnetic arrangement (along the c axis) of the ferromagnetic planes (\( \perp c \)).

E. The specific heat of FeBr\(_2\)

The d-electron specific heat is calculated [15] by making use of the general formula [11,12]:

\[
c_d(T) = -T \frac{\delta^2 F(T)}{\delta T^2}
\]

(7)

where \( F(T) \) is the free energy calculated over the available energy states resulting from the consideration of the Hamiltonian (2), with (6) if the magnetically-ordered state is realized.

The paramagnetic susceptibility \( \chi_d(T) \) is evaluated as the induced magnetization by the applied field, say of 1T, provided that the magnetization is linear with the field as is in the present case.

III. RESULTS AND DISCUSSION

Results for the temperature dependence of the specific heat \( c_d(T) \) and of the magnetic susceptibility \( \chi_d(T) \) of the Fe\(^{2+}\)-ion system are shown in Figs 2 and 3, respectively. The parameters used are:

1. the cubic \( B_4 \) parameter is taken as +200 K in order to get the overall crystal-field splitting \( E_g-T_{2g} \) of about 2 eV (\( =120\cdot B_4 \)) - this is for the explanation of the yellow colour of FeBr\(_2\).
2. the spin-orbit coupling $\lambda$ equals -150 K as is given for the Fe$^{2+}$ ion in ref. 13 on p. 399.

3. the trigonal distortion $B_{0}^{0}=-30$ K yields the singlet-doublet splitting of $D=33$ K (2.8 meV) with the doublet lower, see Fig. 1e,

4. the molecular-field coefficient $n= -0.8$ K/µ$_{B}^{2}$ ($=-1.2$ T/µ$_{B}$) has been adjusted in order to reproduce the experimentally observed Neel temperature of 14.2 K.

All these parameters are physically very reasonable. They provide the electronic structure of the Fe$^{2+}$ ion as is shown in Fig. 1. The cubic CEF is responsible for the large energy scale (say, 1.5-4.0 eV) and the s-o coupling for the medium, 25-200 meV, energy scale. The off-cubic distortion causes energetical effects up to 10-15 meV. The magnetic interactions range up to, say, 20 meV for compounds with the high magnetic ordering temperature. In case of FeBr$_{2}$ they are of 1.5 meV only. The inclusion of the relatively weak intersite magnetic $H_{d-d}$ interactions is indispensable for the appearance of the long-range magnetic order. They cause an internal magnetic field, of 5.15 T at 0 K, and a Zeeman-like splitting of the doublet levels. The splitting is strongly temperature dependent and it diminishes at $T_N$. The temperature dependence of the three lowest levels is shown in Fig. 4. These three levels with their temperature dependence are responsible for the low-temperature specific heat. In fact, the $\lambda$-peak dependence is mainly determined by the temperature dependence of the lowest level. Of course, the temperature dependence occurs only in the magnetically-ordered state as the temperature dependence of the CEF levels, if exist, is expected to be negligible provided the crystallographic structure is not changed.

The magnetic-moment value is perfectly reproduced by our calculations. We have obtained a value of 4.26 $\mu_B$ in very good agreement with experimental data [1,2]. It is directed along the hexagonal c axis that is the natural distortion direction (such the distortion does not change the symmetry of the elementary cell, though it changes the local symmetry). Such the direction assures the Ising-like behaviour of the Fe$^{2+}$ ion moment. The present approach allows for the evaluation of the orbital and spin contributions, Fig.5. The $S_z$ value amounts to +1.74 (the spin moment of 3.48 $\mu_B$) whereas the calculated orbital moment
amounts to 0.78 $\mu_B$. It is very large - it amounts to 18% of the total moment. (On the other hand sceptists can say that it is only 39% of the full orbital moment of 2 $\mu_B$.) These studies about the magnetic-moment value and the different effects on the fine electronic structure indicate that the orbital moment has to be "unquenched" in the solid-state physics. It turns out that the trigonal distortion is much more effective in the unquenching of the orbital momentum than the tetragonal distortion, for instance.

This large orbital contribution is also seen in the temperature dependence of the paramagnetic susceptibility. The effective moment of 5.39 $\mu_B$, calculated from the $\chi^{-1}$ vs T plot at room temperature, exceeds by 11% the spin-only moment. However, one should notice in Fig. 3 that the general course of the calculated susceptibility differs substantially from the S=2 plot. Our calculated moment is in very good agreement with typical values often found in Fe$^{2+}$-ion compounds [Ref.9, Table 14.2; Ref.10, Table 31.4]. Such the increase is attributed in the effective approaches to the change of the g factor; instead of 2 it would be 2.20 at the present case. Inspecting further the $\chi(T)$ curve in Fig. 3 one notices that $\chi(T)$ is not the straight line. The low-temperature behaviour indicates an even larger value for the effective moment. Indeed, the slope in the 40-100 K range yields 6.58 $\mu_B$ pointing to the almost full orbital contribution (6.70 $\mu_B$).

The found molecular-field coefficient $n$ of 1.2 T/$\mu_B$, determining the magnetic-ordering temperature, indicates that 2/3 of its is related with antiferromagnetic interactions as a value of 0.8 T/$\mu_B$ is derived from the metamagnetic field of 3.15 T.

IV. CONCLUSIONS

Temperature dependence of the specific heat and of the magnetic susceptibility of FeBr$_2$ as well as the zero-temperature magnetic moment and its direction have been surprisingly well described as originating from low-energy localized states of the Fe$^{2+}$ ions. The present approach provides the consistent physical description of the electronic structure in the 0-4 eV energy range. The obtained good agreement indicates extremely strong correlations of
the six 3d electrons in the Fe$^{2+}$ ion confirming the validity of the Russel-Saunders scheme and Hund’s rules. These calculations show that for the meaningful analysis of electronic and magnetic properties of FeBr$_2$ the spin-orbit coupling is essentially important and that the orbital moment is largely ”unquenched” (by the off-cubic trigonal distortion in the presence of the spin-orbit coupling). The 18% orbital contribution proves the unapplicability of all approximate treatments of the Hamiltonian (1) both in terms of an effective $S$ ($≠ 2$) and a fictitious orbital $L$ ($≠ 2$) number. The calculated effective moment of 5.39$\mu_B$ at room temperature, exceeding by 10% the spin-only moment, is in perfect agreement with typical values often found in Fe$^{2+}$-ion compounds. This remarkably good and consistent description proves a posteriori that the fine quasi-atomic electronic structure, resulting from the crystal-field and spin-orbit coupling, survives in the solid-state matter.

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[15] the computer program is available on the written request to the author.

**Figure captions:**

Fig. 1. The fine electronic structure of the highly-correlated $3d^6$ electronic system. a) the 25-fold degenerated $^5D$ term given by Hund’s rules: $S=2$ and $L=2$. b) the effect of the cubic octahedral crystal-field, c) the combined action of the spin-orbit coupling and the cubic crystal field: $B_4=+200K$, $\lambda=-150 K$; d and e) an extra splitting produced by the trigonal distortion - the case e is realized in FeBr$_2$; the trigonal-distortion parameter $B_2^0=-30K$ produces a spin-like gap of 2.8 meV.

Fig. 2. The calculated temperature dependence of the specific heat of FeBr$_2$ (the solid line) as composed from the lattice contribution, shown by the dashed-point line, and the d-electron contribution with the $\lambda$ peak at $T_N$. Points represent experimental data after Ref. 3.

Fig. 3. The calculated temperature dependence of the paramagnetic susceptibility of the Fe$^{2+}$ ion in the slightly-distorted octahedral crystal field (the solid line). The dashed line shows the susceptibility for the exactly octahedral crystal field and the spin-orbit coupling. Points represent experimental data for FeBr$_2$ [6, p. 58].

Fig. 4. Temperature dependence of the three lowest levels showing the splitting of the lowest doublet in the magnetic state (below $T_N=14.2K$). The collapse of the splitting of the
ground-state doublet should be noticed.

Fig. 5. The calculated temperature dependence of the local magnetic moment of the Fe$^{2+}$ ion in FeBr$_2$ together with spin and orbital contributions at 0 K.
$T_{2g} \quad E_g \approx 2.2 \text{ eV}$

$\frac{120}{B_4}$

$Fe^{2+}$ in $FeBr_2$

octahedral

$B_4 = +200 \text{ K}$

$\lambda = -150 \text{ K}$

$D_{5\cdot5}$

$L = 2$

$S = 2$

$trigonal$

distortion

$B_2^0 > 0 \quad B_2^0 < 0$

$a) \quad b) \quad c) \quad d) \quad e)$
\[ B_2 = +200 \text{ K} \]
\[ B_2^0 = -30 \text{ K} \]
\[ n = -0.8 \text{ K} \]
\[ \lambda = -150 \text{ K} \]

Fe\(^{2+}\) ion in FeBr\(_2\)

\( d^6 \) system
pseudo-cubic octa trigonal

\[ c (\text{J/K mol}) \]

\[ T (\text{K}) \]
\[ \chi(\mu_B/T \text{ ion}) = S = 2 \]

\[ \chi'(\mu_B/T \text{ ion}) = \lambda \]

\[ B_4 = +200 \text{ K} \]

\[ \lambda = -150 \text{ K} \]

\[ B_2^0 = -30 \text{ K} \]

\[ B_2^0 = 0 \text{ K} \]

\[ \parallel \text{c exp.} \]

\[ \perp \text{c} \]
Fe$^{2+}$ ion in FeBr$_2$

-10040
0 $\mu_B$
singlet

-10080
-4.2 $\mu_B$
doublet

-10120
4.3 $\mu_B$

B$^d_4$ = +200 K
B$_2$ = -30 K
n = -0.8 K
\lambda_c = -150 K

T$_N$
$\text{Fe}^{2+}$ ion in FeBr$_2$

d$^6$ system
pseudo-cubic octa trigonal

$B_2 = +200$ K
$B_3^0 = -30$ K
$n = -0.8$ K
$\lambda = -150$ K