Large Orbital Magnetic Moment and Coulomb Correlation effects in FeBr$_2$

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We have performed an all-electron fully relativistic density functional calculation to study the magnetic properties of FeBr$_2$. We show for the first time that the correlation effect enhances the contribution from orbital degrees of freedom of $d$ electrons to the total magnetic moment on Fe$^{2+}$ as opposed to common notion of nearly total quenching of the orbital moment on Fe$^{2+}$ site. The insulating nature of the system is correctly predicted when the Hubbard parameter $U$ is included. Energy bands around the gap are very narrow in width and originate from the localized Fe-$3d$ orbitals, which indicates that FeBr$_2$ is a typical example of the Mott insulator.

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FeX$_2$(X= Cl, Br, I) are well known model systems for the study of antiferromagnetism. They show unusual metamagnetic behavior wherein they undergo a phase transition from the antiferromagnetic to a saturated paramagnetic phase as a function of external magnetic field and temperature. FeBr$_2$ has a layered structure, where the ferromagnetic Fe layers are widely separated by non-magnetic halogen layers producing a quite weak interlayer antiferromagnetic interactions ($T_N= 14.2$ K). The long range antiferromagnetic ordering can be overcome by applying an external magnetic field ($\sim 30$ kOe) parallel to the $c$-axis. As a result, many theoretical and experimental works on FeBr$_2$ have been concentrated on probing the axial magnetic phase diagram, to predict and understand anomalies near the antiferromagnetic to the paramagnetic phase boundary.

In addition, the electronic structures of transition metal dihalide system are of interest because they show various types of interesting behavior due to the strong correlation effect in the transition metal ion. For example, they behave as a Mott insulator or charge transfer type insulator depending upon the relative size of charge transfer energy $\Delta$ and the intra-orbital correlation energy $U$ of the $d$-electrons.

Although large amount of work is done to understand the anomalies in the phase diagram and the correlation effects, surprisingly no electronic structure is known from the first principles calculation. In this report, we study the electronic and magnetic properties of one of these systems (FeBr$_2$) by combining a first principles method and the Hubbard on-site correlation term.

Orbital magnetic moment plays a crucial role in determining many important effects in magnetic materials such as magnetic crystalline anisotropy, non-collinear magnetism, magneto-optical Kerr effect etc. It is a well known fact that crystal field interaction quenches the orbital magnetic moment in systems containing 3d-transition metal. Accordingly, it is assumed that because of strong crystalline field on Fe$^{2+}$ ions from the surrounding Br$^{-}$, the orbital moment will also get quenched in FeBr$_2$. Ropka, Michalski, and Radwanski showed that the orbital moment is not quenched fully by the crystal field through their quasi-atomic calculation. Ropka et al. ascribed the origin of the large orbital moment to spin-orbit coupling (SOC). Our study also demonstrates that orbital degrees of freedom has substantial contribution (of $\sim 20\%$ to the total magnetic moment). However, correlation effect in Fe 3d orbitals increases the orbital contribution to the total magnetic moment significantly, as discussed below. This is explicitly shown by incorporating the Hubbard parameter $U$ in the self-consistent calculation which also predict an insulating nature.

FeBr$_2$ is isomorphic to the hexagonal CdI$_2$ structure (space group $p3m1$, $D_{3d}^3$. No. 164) at atmospheric pressure and low temperature. Figure 1 shows the crystal structure. The lattice parameters are $a = 3.77$ Å and $c = 6.22$ Å where the $c/a$ ratio ($\sim 1.65$) is very close to the ideal value of $\sqrt{8/3} \sim 1.63$. The chemical unit cell has one Fe and two Br atoms. The Br atoms are bonded

![FIG. 1: Crystal structure of FeBr$_2$. Black and white spheres represent Fe and Br atoms, respectively.](image-url)
tightly to the Fe atoms on either side by covalent bond to form a Br-Fe-Br trio. The Br-Fe-Br trios are separated by an empty layer between them, and bonding between the trios is a weak van der Waals type. The Fe ions are located at 1a positions whereas Br atoms are located at 2d positions in a unit cell. Each Fe ion is at the center of octahedron formed by the surrounding Br ions with a small distortion. As a result, a small trigonal component of crystal field due to this distortion is present apart from the cubic component. FeBr$_2$ is also taken as an example of dynamic Jahn-Teller system wherein strong coupling between lattice and spin excitations are manifested in temperature dependent Raman spectrum.\[2\]

We have carried out density functional calculations\[3\] on FeBr$_2$ using the full-potential linear muffin-tin orbital (FPLMTO)\[4\] method with full relativistic effects on the single-particle electron states and the nonrelativistic local density approximation (LDA) for the many-body effects in the exchange-correlation energy with the Vosko-Wilk-Nussair form.\[5\] The strong correlation effect in the Fe 3d site is taken into account by LDA+U method.\[6\] In the past, LDA+U method is frequently used to predict the occurrence of large orbital moment and insulating nature and is found to be a robust method for the correlated systems.\[7\] The chemical unit cell is doubled ($c = 12.44$ Å) along c-axis to simulate the antiferromagnetic system with 2 Fe atoms and 4 Br atoms. Basis functions, electron densities and potential were calculated without any shape approximation. The trial wave function, potential and charge densities are expanded in combination of spherical harmonics ($l_{max} = 6$) inside the atomic muffin-tin sphere region and plane wave Fourier series in the interstitial region ($E_{cut}=94$ Ry). 2 $\kappa$-basis set (where $\kappa$ is kinetic energy of muffin-tin orbitals in interstitial region) is used. In the Fe sphere, 4s, 4p and 3d orbitals are taken as valence states and 3p orbitals are treated as semi-core state, whereas in the Br sphere, 3d orbitals are taken as a semicore state and 4s, 4p and 4d orbitals are taken as valence states. The semicore states are treated in a separate energy window. The k-space integration is done with 30 k-points in irreducible part of Brillouin Zone(IBZ)(144 k-points in full Brillouin Zone(FBZ)) using the tetrahedron method.\[7\] We have also carried out calculations with larger set of k-points (43 points in IBZ and 320 points in FBZ), but the total energies are found to be converged within 1 meV and magnetic moments change within 0.01 $\mu_B$. To bring about the orbital contribution to total magnetic moment, spin-orbit interaction is included in the crystal Hamiltonian. The calculations are done at experimental lattice constant.

Due to mean field character of LDA, it incorrectly describes the ground state of many strongly correlated materials, for example, the transition metal oxide systems.\[8\] In these materials, the d-orbitals are well localized and retain the strong atomic-like character. For a good description of strong on-site correlation effect between electrons in the d-shell, the LDA+U method is widely used. This method identifies these orbitals as correlated states. The LDA+U variational total energy functional takes the form

$$E^{tot}[\rho, \hat{n}] = E^{LDA}[\rho] + E^{U}[\hat{n}] - E^{dc}[\hat{n}],$$  

where the first term is the usual local spin density functional of the local electron spin density $\rho^{\sigma}(\mathbf{r}) (\sigma = \uparrow, \downarrow)$. $\hat{n}^{\sigma}$ is a local orbital (d or f) occupation matrix. $E^{U}$ is an electron-electron interaction energy which depends on Slater integrals $F^{0}$, $F^{2}$ and $F^{4}$. $E^{dc}$ is a double counting term. The Slater integrals are in turn related to the screened Coulomb and exchange parameters U and J respectively:

$$J = \frac{F^{4} + F^{2}}{14} \tag{2}$$

and

$$U = F^{0}. \tag{3}$$

For 3d electron systems it is found that $F^{2}/F^{4} = 0.625$. It is to be noted that the orbital polarization is automatically included in LDA+U method, as the orbital dependent effect comes from $F^{2}$ and $F^{4}$. Since no experimental value of U in FeBr$_2$ system is available in the literature, we decided to take U and J values from experiments on other systems. It is to be noted that the experimental value of U in FeO system is 5.7 eV and 6.0 eV. In similar systems like antiferromagnetic transition metal oxides,\[9\] J is close to 0.9 eV and does not change much from this value, so we have taken $J = 0.9$ eV. To check the validity of our U values, we performed the self-consistent calculations at four different values of U, namely, 5.7 eV, 6.0 eV, 6.4 eV and 6.8 eV. We consistently obtain the insulating ground state in agreement with the experiment, although the energy gap changes by a small fraction. The magnetic moments are almost constant with respect to the U values. So, the four different values of U do not affect our conclusions. We present our results for U = 6

| $E_{g}^{\uparrow}$ | $E_{g}^{\downarrow}$ | $\mu$ | $\mu_s$ | $\mu$ |
|---|---|---|---|---|
| 2.0$^a$ | 0.0 | 1.76 | 1.87 |
| 0.0 | 1.43 | 1.53 |
| 0.14 | 0.66 | 0.66 |
| 3.50 | 3.85 | 3.86 |
| 4.4$^a$ | 3.64 | 4.51 | 4.52 |

$^a$Reference [9]
$^b$Reference [8]
eV taken from the experimental value in FeO system if not mentioned explicitly.

Table I shows energy gap and magnetic moment for FeBr₂ at the two representative values of U. LDA and GGA both predict FeBr₂ to be metallic, while LDA+U predicts it to be insulating in agreement with experiment. It is, therefore, crucial to take into account the correlation effects to obtain the correct electronic structure. It means that there is a strong intra-orbital correlation for Fe²⁺ ion in FeBr₂ and that this strong correlation is responsible for the insulating nature.

Figure 2 shows dispersion curves for electronic states along high symmetry directions in IBZ of the hexagonal unit cell. The top of valence band is set to energy zero. Br-4s bands are not shown in the figure which is located at around -16 eV. It is seen from Fig. 2 that there is an indirect energy gap between H and Γ with a gap size of 1.53 eV. A direct gap of 1.87 eV is located at the middle of the symmetry line connecting M and Γ. No experimental value of the gap is available in the literature. However, since FeBr₂ is yellow in color, the gap would be around 2 eV which may correspond to a transition across the direct gap. Our calculated gap values of 1.87 eV are in reasonable agreement with the conjectured one (see Table 1). We can see from Fig. 2 that the bands have little dispersion in the z-direction (see the bands along symmetry lines Γ-A, L-M, and K-H) which is a characteristic feature in systems with layered structure like graphite or some high Tc superconductors. The equienergy surfaces near the energy gap, therefore, have cylinder-like shapes.

Density of states (DOS) of FeBr₂ in Fig. 3(a) shows the total DOS for FeBr₂. Spin-up Fe-d states are located deep in energy between -10 eV and -6.5 eV, whereas spin-down Fe-d states are located at around -0.5 eV and 3 eV as shown in Fig. 3(b). Fe-d orbitals form localized states with narrow band width where the main peaks are located -9.6 eV, -8.9 eV, -6.8 eV for spin-up states and -0.2 eV, 1.6 eV, 2.2 eV for spin-down states. A group of bonding orbitals with wide band width is located between -6 eV and -2 eV which is the hybridization of Br-p and Fe-s bands (Fig. 3(c)). This wide band gives a covalent bonding within the Br-Fe-Br trio. The energy gap between the hybridized bonding orbitals of Br-p/Fe-s and the conduction band is 3.6 eV. The d-bandwidth, W, of 0.5 eV is found to be much smaller than U so that U/W > 1. The states near the band gap at conduction band minimum and valence band maximum are mainly from spin-down Fe-d states. This means that FeBr₂ is a typical Mott insulator (materials in which the kinetic energy gain is smaller than the Coulomb repulsion energy U and as a result electrons can hardly hop to the Fe-d orbitals).

Fe²⁺ ion in FeBr₂ has six electrons in d orbitals. The nearly octahedral arrangement of Br⁻ surrounding Fe²⁺ ions introduces crystal field which splits the d-orbital into t₂g (dₓ²-y², d₃z²-r², and dₓz) and e₉ (dₓ²-y² and d₃z²-r²) orbitals. This splitting hinders the free rotation of the electrons and reduces its orbital moment. Both t₂g and e₉ orbitals of spin-up Fe-d bands are fully occupied while only one of t₂g orbitals is occupied in spin-down bands...
to contribute $4 \mu_B$ as a spin contribution to the total magnetic moment. This simple estimation of the magnetic moment from DOS is consistent with the calculated spin contribution of 3.86 $\mu_B$ to the total magnetic moment. The Fe$^{2+}$ ion has $L=2$, $S=2$ and $J=4$ in free space. If we assume that the orbital moment is quenched as in usual 3d transition metal magnetic system, the spin contribution to the total magnetic moment is also consistent with the simple atomic picture. However, the neutron diffraction study shows that the magnetic moment on Fe site is nearly 4.4 $\mu_B$. Wilkinson et al. argue that this moment is close to that expected for divalent metallic Fe$^{2+}$ ions if the orbital contribution is taken to be zero. Our calculation shows that total magnetic moment $\mu$ is split into orbital $\mu_1$ and spin parts $\mu_s$ with the orbital part contributing a significant amount. From Table I it is seen that the orbital contribution to the total magnetic moment is $\sim 20\%$ the total magnetic moment. It is interesting to note that the nearly octahedral arrangement of Br ions surrounding Fe ion is not able to totally quench the orbital degrees of freedom. The orbital and spin degrees of freedom are therefore not totally decoupled (obeying Hund’s third rule). Quasi-atomic calculations by Ropka et al. also give the orbital moment close to our values, and the large orbital moment were speculated to be due to SOC. However, our calculations show that SOC is not enough to explain the large orbital contribution as can be seen in table II. LDA calculation with SOC gives an orbital magnetic moment of 0.14 $\mu_B$ and total magnetic moment of 3.64 $\mu_B$ which is smaller than the experimental value of 4.4 $\mu_B$. When we include the on-site correlation effect at the Fe site as well as SOC, we get about five times larger orbital magnetic moment of 0.66 $\mu_B$. Total magnetic moment of 4.52 $\mu_B$ is in good agreement with experimental value within 3% error. We can see that the important contribution to the large orbital magnetic moment of FeBr$_2$ is mostly due to the correlation effect of the 3d orbitals. Therefore, the correlation effect plays a very important role in determining the magnetic properties as well as the insulating ground state. In Ropka et al.’s quasi-atomic model, the correlation effects are included by the correlated basis set with no explicit term representing on-site correlation effect in the Hamiltonian. However, in our calculation we include explicitly the correlation term in the Hamiltonian.

We suggest that, if an x-ray magnetic circular dichroism (XMCD) experiment, which is a local probe for spin and orbital magnetic contribution to total magnetic moment, is performed on FeBr$_2$, then the orbital contribution can easily be probed. Such experiments relate, via atomic sum rules, the dichroic intensities (i.e., difference between right- and left-circularly polarized photons absorption cross-sections) measured at the absorption edges of the constituent elements to the ground-state expectation value of effective one-electron operators such as $\langle L^2 \rangle$ and $\langle S^2 \rangle$.

To conclude, we have shown for the first time that the correlation effect is important in describing the magnetic and electronic properties of FeBr$_2$ which plays an important role in enhancing the orbital magnetic moment and predicting the correct insulating nature. This indicates that Fe$^{2+}$ ion in FeBr$_2$ retains to some extent its atomic-like character. FeBr$_2$ can be classified as a typical example of Mott insulator due to the character of the energy gap and the width of the bands around the gap. We expect that the present calculation will help understand the electronic and magnetic properties of other iron halide systems.

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