

Large orbital magnetic moment and Coulomb correlation effects in FeBr₂

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We have performed an all-electron fully relativistic density-functional calculation to study the magnetic properties of FeBr₂. We show that the correlation effect enhances the contribution from orbital degrees of freedom of *d* electrons to the total magnetic moment on Fe²⁺, as opposed to the common notion of a nearly total quenching of the orbital moment on the Fe²⁺ 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-3*d* orbitals, which indicates that FeBr₂ is a typical example of a Mott insulator.

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FeX₂ (*X*=Cl,Br,I) is a well-known *model* system for the study of antiferromagnetism.¹ It shows an unusual *metamagnetic* behavior wherein it undergoes a phase transition from an antiferromagnetic phase to a saturated paramagnetic phase as a function of external magnetic field and temperature. FeBr₂ has a layered structure, where the ferromagnetic Fe layers are widely separated by nonmagnetic halogen layers, producing quite a weak interlayer antiferromagnetic interaction (*T_N*=14.2 K). The long-range antiferromagnetic ordering can be overcome by applying an external magnetic field (~30 kOe) parallel to the *c* axis.² As a result, many theoretical³ and experimental^{4,5} works on FeBr₂ concentrated on probing the axial magnetic phase diagram, to predict and understand anomalies near the antiferromagnetic to paramagnetic phase boundary.

In addition, the electronic structure of a transition-metal dihalide system is of interest because such systems show various types of interesting behavior due to the strong correlation effect in the transition-metal ion.⁶ For example, they behave as Mott insulators or charge-transfer-type insulators depending upon the relative size of charge transfer energy Δ and the intraorbital correlation energy *U* of the *d* electrons.

Although a large amount of work was done to understand the anomalies in the phase diagram and the correlation effects, surprisingly no electronic structure is known from first-principles calculations. In this paper, we study the electronic and magnetic properties of one of these systems (FeBr₂) by combining a first-principles method and a Hubbard on-site correlation term.

The orbital magnetic moment plays a crucial role in determining many important effects in magnetic materials such as magnetic crystalline anisotropy, noncollinear magnetism, the magneto-optical Kerr effect, etc.⁷ It is a well-known fact that crystal-field interaction quenches the orbital magnetic moment in systems containing 3*d* transition metals. Accordingly, it is assumed that, due to a strong crystalline field on Fe²⁺ ions from the surrounding Br⁻, the orbital moment will also be quenched in FeBr₂.⁸ Ropka, Michalski, and Radwanski⁹ showed through their quasiautomatic calculation that the orbital moment is not fully quenched by a crystal field. 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 makes a substantial contribution (of ~20% to the total magnetic moment). However, the correlation effect in Fe 3*d* 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 a self-consistent calculation, which also predicts an insulating nature.

FeBr₂ is isomorphic to the hexagonal CdI₂ structure (space group *p* $\bar{3}m1$, *D*_{3*d*}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 (Ref. 8), where the *c/a* ratio (~1.65) is very close to the ideal value of $\sqrt{8/3}$ ~1.63. The chemical unit cell has one Fe atom and two Br atoms. The Br atoms are bonded tightly to the Fe atoms on either side by a 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 of weak van der Waals type. The Fe ions are located at 1*a* positions, whereas Br atoms are located at 2*d* positions in a unit cell. Each Fe ion is at the center of octahedron formed by the

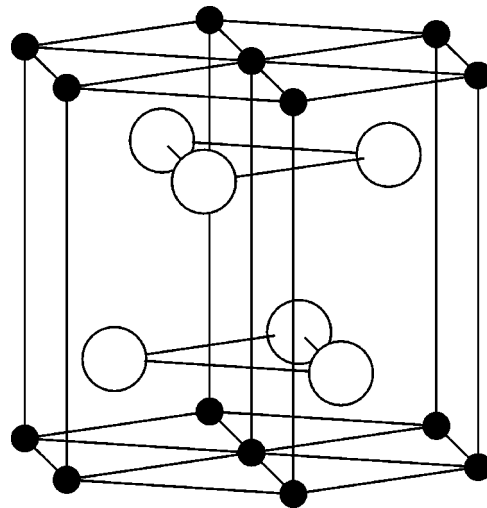


FIG. 1. Crystal structure of FeBr₂. Black and white spheres represent Fe and Br atoms, respectively.

surrounding Br ions with a small distortion. As a result, a small trigonal component of the crystal field due to this distortion is present apart from the cubic component. FeBr₂ was also taken as an example of a dynamic Jahn-Teller system, wherein strong couplings between lattice and spin excitations are manifested in a temperature-dependent Raman spectrum.¹⁰

We have carried out density-functional calculations¹¹ on FeBr₂ using the full-potential linear muffin-tin orbital¹² method with full relativistic effects on the single-particle electron states, and the nonrelativistic local-density-approximation (LDA) for many-body effects in the exchange-correlation energy with the Vosko-Wilk-Nussair form.¹³ The strong correlation effect in the Fe 3*d* site is taken into account by a LDA+*U* method.¹⁴ In the past, the LDA+*U* method was frequently used to predict the occurrence of large orbital moments and insulating nature, and was found to be a robust method for correlated systems.^{15,16} The chemical unit cell is doubled ($c = 12.44 \text{ \AA}$) along the *c* axis to simulate an antiferromagnetic system with two Fe atoms and four Br atoms. Basis functions, electron densities, and potentials were calculated without any shape approximation. The trial wave function, potentials, and charge densities are expanded in combinations of spherical harmonics ($L_{max} = 6$) inside the atomic muffin-tin sphere region and plane-wave Fourier series in the interstitial region ($E_{cut} = 94 \text{ Ry}$). Two κ -basis set (where κ is the kinetic energy of muffin-tin orbitals in the interstitial region) is used. In the Fe sphere, 4*s*, 4*p*, and 3*d* orbitals are taken as valence states, and 3*p* orbitals are treated as semicore states, whereas in the Br sphere, 3*d* orbitals are taken as semicore states and 4*s*, 4*p*, and 4*d* orbitals are taken as valence states. The semicore states are treated in a separate energy window. The \mathbf{k} -space integration is done with 30 \mathbf{k} points in irreducible part of the Brillouin zone (IBZ) [144 \mathbf{k} points in the full Brillouin zone (FBZ)] using the tetrahedron method.¹⁷ We have also carried out calculations with larger set of \mathbf{k} points (43 points in the IBZ and 320 points in the FBZ), but the total energies are found to converge within 1 meV and the magnetic moments to change within $0.01\mu_B$. To bring about an orbital contribution to the total magnetic moment, spin-orbit interaction is included in the crystal Hamiltonian. The calculations are done at an experimental lattice constant.

Due to the mean-field character of the LDA, it incorrectly describes the ground state of many strongly correlated materials, for example, transition-metal oxide systems.¹⁸ In these materials, the *d* orbitals are well localized, and retain a strong atomiclike character. For a good description of strong on-site correlation effects 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

$$E^{tot}[\rho, \hat{n}] = E^{LDA}[\rho] + E^U[\hat{n}] - E^{dc}[\hat{n}], \quad (1)$$

where the first term is the usual local-spin-density functional of the local spin density $\rho^\sigma(\mathbf{r})$ ($\sigma = \uparrow, \downarrow$). \hat{n}^σ 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

TABLE I. Direct energy gap (E_g^d), indirect energy gap (E_g^i), orbital magnetic moment (μ_l), spin magnetic moment (μ_s), and total magnetic moment $\mu = \mu_l + \mu_s$ for FeBr₂. The energy gap is in eV and magnetic moments are in Bohr magneton. $U = 0 \text{ eV}$ in LDA calculation.

	Expt.	LDA($U=0$)	$U=5.7$	$U=6.0$
E_g^d	2.0 ^a	0.0	1.76	1.87
E_g^i		0.0	1.43	1.53
μ_l		0.14	0.66	0.66
μ_s		3.50	3.85	3.86
μ	4.4 ^b	3.64	4.51	4.52

^aReference 9.

^bReference 8.

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:

$$J = \frac{F^4 + F^2}{14} \quad (2)$$

and

$$U = F^0. \quad (3)$$

For 3*d* electron systems it is found that $F^2/F^4 = 0.625$. It should be noted that the orbital polarization is automatically included in LDA+*U* method,¹⁵ as the orbital-dependent effect comes from F^2 and F^4 . Since no experimental value of U in FeBr₂ system is available in the literature, we decided to take U and J values from experiments on other systems. The experimental values of U in an FeO system¹⁹ are 5.7 and 6.0 eV. In similar systems such as antiferromagnetic transition-metal oxides,¹⁴ J is close to 0.9 eV, and does not change much from this value, thus we have taken $J = 0.9 \text{ eV}$. To check the validity of our U values, we performed self-consistent calculations at four different values of U , namely, 5.7, 6.0, 6.4, and 6.8 eV. We consistently obtained an insulating ground state, in agreement with the experiment, although the energy gap changed by a small fraction. The magnetic moments are almost constant with respect to the U values. Thus the four different values of U do not affect our conclusions. We present our results for $U = 6 \text{ eV}$ taken from the experimental value in an FeO system if not mentioned explicitly.

Table I shows the energy gap and magnetic moment for FeBr₂ at two representative values of U . The LDA and the generalized gradient approximation both predict FeBr₂ to be metallic, while the LDA+*U* theory predicts it to be insulating in agreement with experiment.⁸ It is, therefore, crucial to take correlation effects into account to obtain the correct electronic structure. This means that there is a strong intra-orbital correlation for the 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 the IBZ of the hexagonal unit cell. The top of the valence band is set to energy zero.

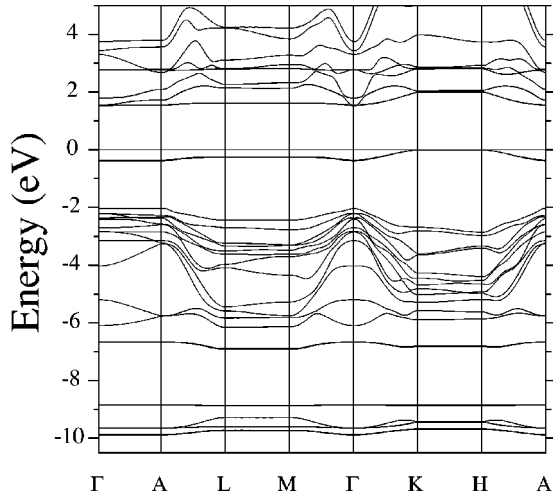


FIG. 2. Energy-band structure of FeBr_2 at $U=6.0$ eV along high symmetry directions in the IBZ of the hexagonal unit cell. The top of the valence band is set to energy zero.

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 FeBr_2 is yellow in color,⁹ the gap would be around 2 eV, which may correspond to a transition across a direct gap. Our calculated gap value of 1.87 eV is in reasonable agreement with the conjectured one (see Table I). 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- T_c superconductors. The equienergy surfaces near the energy gap, therefore, have cylinderlike shapes.

The density of states (DOS) of FeBr_2 in Fig. 3(a) shows the total DOS for FeBr_2 . Spin-up Fe- d states are located deep in energy between -10 and -6.5 eV, whereas spin-down Fe- d states are located at between -0.5 and 3 eV, as shown in Fig. 3(b). Fe- d orbitals form localized states with narrow bandwidths where the main peaks are located at -9.6 , -8.9 , and -6.8 eV for spin-up states and at -0.2 , 1.6, and 2.2 eV for spin-down states. A group of bonding orbitals with wide bandwidths is located between -6 and -2 eV, which is a 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 -band-width 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 the conduction-band minimum and the valence-band maximum are due mainly to spin-down Fe- d states. This means that FeBr_2 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).

The Fe^{2+} ion in FeBr_2 has six electrons in d orbitals. The

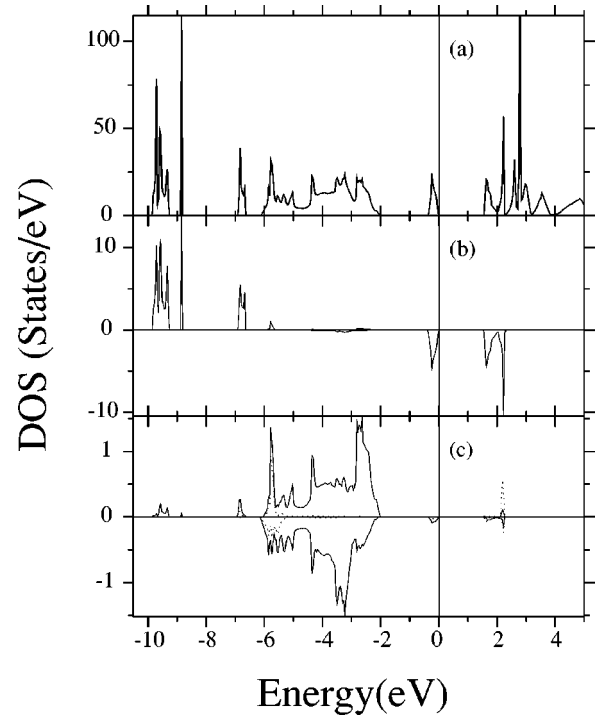


FIG. 3. Density of states for FeBr_2 . (a) Total DOS. (b) Partial DOS of Fe-3d states. (c) Partial DOS of Br-4p (solid line) and Fe-4s (dotted line). In (b) and (c), positive and negative DOS's represent spin-up and -down DOS's, respectively.

nearly octahedral arrangement of Br^- surrounding Fe^{2+} ions introduces a crystal field, which splits the d orbital into t_{2g} (d_{xy} , d_{yz} , and d_{zx}) and e_g ($d_{x^2-y^2}$ and $d_{3z^2-r^2}$) orbitals. This splitting hinders the free rotation of the electrons and reduces its orbital moment. Both t_{2g} and e_g orbitals of spin-up Fe- d bands are fully occupied, while only one of the t_{2g} orbitals is occupied in spin-down bands to contribute $4\mu_B$ as a spin contribution to the total magnetic moment. This simple estimate of the magnetic moment from the 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 a typical 3d transition-metal magnetic system, the spin contribution to the total magnetic moment is also consistent with the simple atomic picture. However, a neutron-diffraction study⁸ showed that the magnetic moment on an Fe site is nearly $4.4\mu_B$. Wilkinson *et al.*⁸ argued 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 μ is split into orbital μ_l and spin μ_s parts, with the orbital part contributing a significant amount. From Table I it is seen that the orbital contribution to the total magnetic moment is $\sim 20\%$ of the total magnetic moment. It is interesting to note that the nearly octahedral arrangement of Br ions surrounding the 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). Quasiatomic calculations of Ropka *et al.*⁹ also gave an orbital moment close to our values, and the large orbital mo-

ment was 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 I. A LDA calculation with SOC gives an orbital magnetic moment of $0.14\mu_B$ and a 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 obtain an orbital magnetic moment of $0.66\mu_B$, about five times larger. The total magnetic moment of $4.52\mu_B$ is in good agreement with the experimental value within a 3% error. Thus we can see that the important contribution to the large orbital magnetic moment of FeBr₂ 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 quasiatomic model, the correlation effects are included by a correlated basis set with no explicit term representing the on-site correlation effect in the Hamiltonian. However, in our calculation we explicitly include the correlation term in the Hamiltonian.

We suggest that if an x-ray magnetic circular dichroism²⁰ experiment, which is a local probe for spin and orbital magnetic contribution to the total magnetic moment, is performed on FeBr₂, then the orbital contribution can easily be

probed. Such experiments via atomic sum rule relate the dichroic intensities (i.e., the difference between right and left circularly polarized photon 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 $\langle L_z \rangle$ and $\langle S_z \rangle$.

To conclude, we have shown that the correlation effect is important in describing the magnetic and electronic properties of FeBr₂, which plays an important role in enhancing the orbital magnetic moment and predicting the correct insulating nature. This indicates that an Fe²⁺ ion in FeBr₂ retains its atomiclike character to some extent. FeBr₂ can be classified as a typical example of a 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 one to understand the electronic and magnetic properties of other iron halide systems.

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