

Many-Electron Model of Band Structure and Metal–Insulator Transition under Pressure in FeBO₃

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A many-electron model is proposed for the band structure of FeBO₃ with regard to strong electron correlations in the d^4 , d^5 , and d^6 configurations. Under normal conditions, FeBO₃ is characterized by a dielectric charge-transfer gap in the strong correlation regime $U \gg W$. With increasing pressure, not only does the d -band W width grow but simultaneously the effective Hubbard parameter U_{eff} sharply drops, which is due to the crossover of high-spin and low-spin ground state terms of the Fe²⁺, Fe³⁺, and Fe⁴⁺ ions. It is predicted that a transition from the semiconducting antiferromagnetic state to the metallic paramagnetic state will occur in the high-pressure phase with increasing temperature. © 2003 MAIK “Nauka/Interperiodica”.

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1. A first-order phase transition from the magnetic to nonmagnetic state of FeBO₃ was observed at the pressure $P_c = 46$ GPa in a series of recent works [1–3]. This transition was accompanied by the structural transition with a 8.6% decrease in volume. A number of indirect data point to the metallization of the system at $P > P_c$; however, no ultimate clarity in the problem of magnetic and electric properties in the high-pressure phase has been achieved so far. From the general point of view, the metallization and the disappearance of localized magnetic moments with increasing pressure are not surprising, because the bandwidth W increases and the Mott–Hubbard insulator with $U \gg W$ transforms to the metallic state with $U < W$ [4]. However, in the case of FeBO₃, as in many other real substances, the simple picture based on the Hubbard model becomes complicated because of the presence of a great number of $d(f)$ orbitals.

In this work, a many-electron model is proposed that takes into account all d orbitals and the strong electron correlations of d electrons. The energies of both high-spin and various low-spin terms of the Fe²⁺, Fe³⁺, and Fe⁴⁺ ions were calculated. It turned out that the electron system under normal conditions occurs in the strong electron correlation regime with a dielectric charge-transfer gap, as classified in [5]. As the pressure grows, not only does the band width W change but the splitting of the e_g and t_{2g} electrons in the crystal field Δ increases as well. It is the growth of Δ that is responsible for the crossover of the high-spin ${}^6A_{1g}$ ($S = 5/2$) and low-spin ${}^2T_{2g}$ ($S = 1/2$) terms of Fe³⁺ and high-spin and low-spin terms of Fe²⁺ and Fe⁴⁺. As a result, not only does the collapse of the magnetic moment take place, as was found in [1–3], but a rearrangement of the diagram of the $d^5 \rightarrow d^4$ and $d^5 \rightarrow d^6$ excitations takes place as well, so that the effective Hubbard parameter $U_{\text{eff}} =$

$E(d^6) + E(d^4) - 2E(d^5)$ sharply decreases. In this fact, we see the nontrivial feature of the phase transition in FeBO₃ under pressure.

2. The first-principles one-electron band-structure calculations of FeBO₃ by density functional methods in the local-density approximation [6] and in the generalized gradient approximation [7] and also the molecular orbital calculation of the FeB₆O₆ cluster [8] revealed the following pattern of the electronic structure of FeBO₃. The empty conduction band ϵ_c is mainly formed by the boron s and p states, the valence band top ϵ_v is mainly formed by the oxygen s and p states, and the band gap between them E_{g0} in the antiferromagnetic phase is 2.5 eV [6], which is sufficiently close to an optical absorption edge of 2.9 eV [9]. The d -electron band lies close to the valence band top with the width $2W_d \approx 2.8$ eV and the crystal-field parameter $\Delta \approx 1$ eV [6]. The hybridization of Fe d electrons with O s and p electrons is very small [6, 8], much smaller than in 3d-metal oxides. This is due to a very strong hybridization inside the BO₃ group; in fact, the (BO₃)³⁻ ion is formed, and the oxygen orbitals are closed on boron, which determines the smallness of p – d hybridization. This circumstance significantly simplifies the many-electron model, because one may calculate the d^n ($n = 4, 5$, and 6) terms of iron in the crystal field rather than the terms of the metal–oxygen complex, as in copper oxides [10].

The intraatomic part of the d -electron Hamiltonian can be written as

$$H_{am} = \sum_{\lambda\sigma} \left(\epsilon_{\lambda} n_{\lambda\sigma} + \frac{U_{\lambda}}{2} n_{\lambda\sigma} n_{\lambda\bar{\sigma}} \right) + \sum_{\lambda, \lambda', \sigma} \sum_{\sigma'} (V_{\lambda\lambda'} n_{\lambda\sigma} n_{\lambda'\sigma'} - J_{\lambda\lambda'} a_{\lambda\sigma}^{\dagger} a_{\lambda'\sigma'} a_{\lambda'\sigma}^{\dagger} a_{\lambda\sigma}), \quad (1)$$

where $n_{\lambda\sigma} = a_{\lambda\sigma}^\dagger a_{\lambda\sigma}$, $a_{\lambda\sigma}$ designates the creation operator of a d electron on one of the five orbitals λ with the spin projection σ , $\bar{\sigma} = -\sigma$. The first term describes the atomic d levels in the crystal field, the small uniaxial crystal-field component is neglected, and it is assumed that $\varepsilon(t_{2g}) = \varepsilon_d - 2\Delta/5$ and $\varepsilon(e_g) = \varepsilon_d + 3\Delta/5$. The other terms in Eq. (1) correspond to the Coulomb intraorbital U_λ and interorbital $V_{\lambda\lambda'}$ repulsions and also to the Hund exchange $J_{\lambda\lambda'}$. For the sake of simplicity, we will neglect the orbital dependence of the Coulomb matrix elements considering that there are three parameters U , V , and J related to each other by the known condition $U = 2V + J$.

The energies $E_S(d^n)$ of the lowest levels of the d^n configuration with spin S equal

$$\begin{aligned}
 E_2(d^4) &= 4\varepsilon_d - 3\Delta/5 + 6V - 6J, \\
 E_1(d^4) &= 4\varepsilon_d - 8\Delta/5 + U + 5V - 3J, \\
 E_0(d^4) &= 4\varepsilon_d - 8\Delta/5 + 2U + 5V - 2J, \\
 E_{5/2}(d^5) &= 5\varepsilon_d + 10V - 10J, \\
 E_{3/2}(d^5) &= 5\varepsilon_d - \Delta + U + 9V - 6J, \\
 E_{1/2}(d^5) &= 5\varepsilon_d - 2\Delta + 2U + 8V - 4J, \\
 E_2(d^6) &= 6\varepsilon_d - 2\Delta/5 + U + 14V - 10J, \\
 E_1(d^6) &= 6\varepsilon_d - 7\Delta/5 + 2U + 13V - 7J, \\
 E_0(d^6) &= 6\varepsilon_d - 12\Delta/5 + 3U + 12V - 6J.
 \end{aligned} \tag{2}$$

The one-electron Green's function without regard for interatomic hopping is calculated exactly with the use of the Hubbard X operators $X^{pq} = |p\rangle\langle q|$ constructed on the eigenstates $|q\rangle$ (Eq. (2)). Such functions were calculated for the metals of the iron group in the limit $U \rightarrow \infty$ in the works [11, 12]. In this case, the energy of the d -electron quasiparticles is determined not by the many-electron terms themselves but by their differences

$$\Omega_{ij} = E_i(d^{n+1}) - E_j(d^n). \tag{3}$$

It is these energies that determine the one-electron band structure of the substance along with the s - and p -electron bands of boron and oxygen. As distinct from the ordinary band states, the quasiparticles specified by Eq. (3) have a variable spectral weight determined by the filling factors $F_{ij} = N_i(d^{n+1}) + N_j(d^n)$, where $N_j(d^n)$ is the filling probability of the i th term of the d^n configuration. This probability is calculated self-consistently through the equation for the chemical potential [11–13].

3. In order to relate the quasiparticle energies (3) to the conduction and valence bands, we will make use of

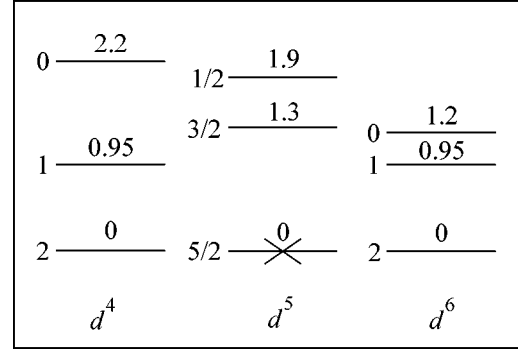


Fig. 1. Diagram of Fe^{4+} , Fe^{3+} , and Fe^{2+} terms; the cross marks the lowest ${}^6A_{1g}$ term filled at $T = 0$. The numbers on the left indicate the spin, and the numbers above indicate the energy (eV) of the term relative to the lowest term for each configuration.

the results of the calculation [6], according to which the valence-band top ε_v coincides with that of the one-electron d band. Thus, we obtain the condition $\varepsilon_v = \varepsilon_d + W_d$. The U and J parameters are found by a comparison of the energies $\Delta E_1 = E_{3/2}(d^5) - E_{5/2}(d^5)$ and with $\Delta E_2 = E_{1/2}(d^5) - E_{5/2}(d^5)$ with exciton peaks at 1.3 and 1.9 eV in the absorption spectra [14]. As a result, we found $U = 1.45$ eV and $J = 0.35$ eV and calculated the energies of all terms given in Eq. (2) (Fig. 1). It is evident in Fig. 1 that, of all the intraatomic d quasiparticles, the transitions $\Omega_v = E_{5/2}(d^5) - E_2(d^4)$, $\Omega'_v = E_{5/2}(d^5) - E_1(d^4)$, and $\Omega''_v = E_{5/2}(d^5) - E_0(d^4)$ with electron annihilation and also $\Omega_c = E_2(d^6) - E_{5/2}(d^5)$, $\Omega'_c = E_1(d^6) - E_{5/2}(d^5)$, and $\Omega''_c = E_0(d^6) - E_{5/2}(d^5)$ with electron creation have a nonzero weight. All Ω_v energies were found to be lower than the valence band top, and Ω_c fell within the gap E_{g0} (Fig. 2). The Ω_c and Ω_v energies are the centroids of the upper and lower Hubbard bands, which are formed if the d - d hoppings t are subsequently taken into account. The effective parameter

$$\begin{aligned}
 U_{\text{eff}} &= \Omega_c - \Omega_v = E_2(d^6) + E_2(d^4) - 2E_{5/2}(d^5) \\
 &= U + 4J - \Delta = 1.85 \text{ eV}.
 \end{aligned} \tag{4}$$

The interatomic hopping in the antiferromagnetic phase is suppressed because of the spin-polaron effect [15]. In the case of hopping between nearest neighbors, the effective hopping integral is determined by the product of the filling factors on two sites belonging to the opposite sublattices A and B [16]. Thus, for the lower Hubbard band, we obtain

$$\begin{aligned}
 t_v^2 &= t^2 (\langle X_A^{+5/2, +5/2} \rangle + \langle X_A^{+2, +2} \rangle) \\
 &\times (\langle X_B^{+5/2, +5/2} \rangle + \langle X_B^{+2, +2} \rangle),
 \end{aligned} \tag{5}$$

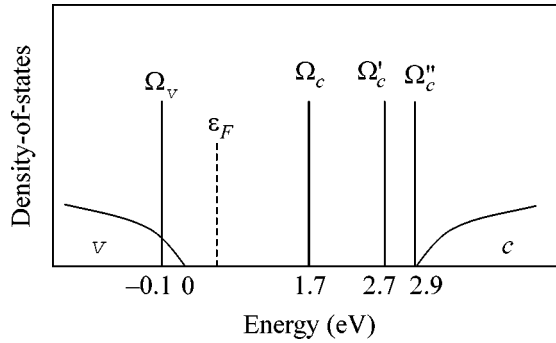


Fig. 2. Diagram of the density of states of FeBO_3 at normal pressure in the antiferromagnetic phase.

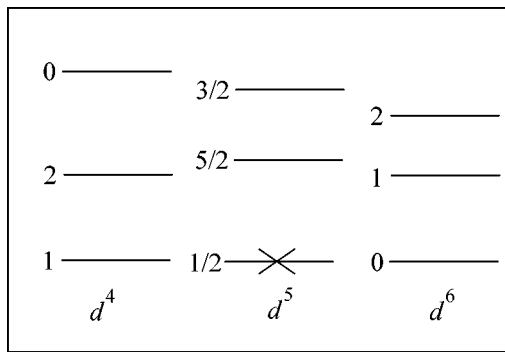


Fig. 3. Diagram of the Fe^{4+} , Fe^{3+} , and Fe^{2+} terms in the high-pressure phase.

where $|+5/2\rangle$ and $|+2\rangle$ are spin sublevels of the $E_{5/2}(d^5)$ and $E_2(d^4)$ terms split in the internal molecular field according to their spin projections. If level $|+5/2\rangle$ is the lowest for sublattice A and is filled, then the lowest level for sublattice B $| -5/2\rangle$ is unfilled at $T = 0$ (with neglect of the zero quantum functions). Therefore, $\langle X_B^{+5/2, +5/2} \rangle = 0$ at $T = 0$, the occupation numbers of all d^4 and d^6 sublevels also equal zero for FeBO_3 , so that the widths of the Hubbard bands are close to zero. This is why the diagram of density of states in Fig. 2 can be compared with the experiment in the antiferromagnetic phase of FeBO_3 . Note that, according to this diagram, FeBO_3 belongs to the class of dielectrics with a gap caused by the charge-transfer processes. In this case, we consider that a hole with the energy ϵ_v is created on oxygen and a d electron with the energy Ω_c is created on iron ($d^5p^6 \rightarrow d^6p^5$ process).

4. As pressure is built up, the crystal-field parameters Δ and the interatomic hopping t increase. The latter, as we can see from Eq. (4), only slightly affects the band structure in the antiferromagnetic phase. The growth of Δ is more important and leads to the crossover of high-spin and low-spin terms. It is evident from

Eq. (2) that, as Δ increases, the $E_{1/2}(d^5)$ term goes down more rapidly than the $E_{3/2}(d^5)$ term; therefore, the crossover with spin $5/2$ takes place for $S = 1/2$. It is this crossover that was observed by the Mössbauer effect in [1–3]. We do not study here the thermodynamics of the system under pressure. This was made in first principles calculations [7]. We are interested in understanding how the crossover is manifested in the electronic structure. Thus, we will consider the high-pressure (HP) phase $P > P_c$, in which $\Delta(P) > \Delta_c = (U + 7J)/2$. The crossover of terms $S = 2$ and $S = 1$ for the d^4 configuration also takes place at this pressure, and the crossover of terms $S = 2$ and $S = 0$ for the d^6 configuration takes place even earlier (at lower pressure). The schematic diagram of many-electron levels in the HP phase is shown in Fig. 3. The rearrangement of all terms leads to a change in the effective Hubbard parameter in the HP phase

$$\begin{aligned} \tilde{U}_{\text{eff}} &= E_1(d^4) + E_0(d^6) - 2E_{1/2}(d^5) \\ &= (U - 3J)/2 = 0.2 \text{ eV}, \end{aligned} \quad (6)$$

so that, along with the growth of the bandwidth, the importance of strong correlations decreases, and we expect the metallization of the system in the paramagnetic phase. Because we do not know the width of the d band, we may speak with confidence only about a tendency toward metallization. Consider two possible variants.

(1) As the band width, we take the result of the band-structure calculation with $W_d = 1.4$ eV. Then, at $U_{\text{eff}} = 0.2$ eV, we expect the metallic paramagnetic state. If the system is characterized by Fermi surface nesting, it will transform into a spin-density-wave state (band ferromagnet) [17–19] with decreasing temperature below

$$T_N = 1.14 W_d \exp\left(-\frac{1}{N(\epsilon_F) U_{\text{eff}}}\right), \quad (7)$$

where $N(\epsilon_F) \sim 1/W_d$ is the density of states at the Fermi level. The electrical properties below T_N are characterized by a dielectric gap $E_g = 2U_{\text{eff}}\langle S^z \rangle$. Assuming that, at $T = 0$, $\langle S^z \rangle = 1/2$ in the HP phase, we obtain $E_g = 0.2$ eV. For T_N , at $U_{\text{eff}} = 0.2$ eV and $W_d = 1.4$ eV, we obtain the estimate $T_N = 10$ K from Eq. (7).

(2) It is possible that the d band is narrower than the overall bandwidth and than U_{eff} . Then the system in the HP phase will remain a Mott–Hubbard insulator and will transform into the metallic state with further growth of the pressure. For the Mott–Hubbard insulator, T_N can be roughly estimated within the effective Heisenberg model with $S = 1/2$. This model in the spin-wave approximation gives [20]

$$T_N = I(0)S(S+1)/3C, \quad (8)$$

where C is the Watson integral and $I(0)$ is the Fourier transform of the interatomic exchange interaction. If

$I(0)$ did not depend on the pressure, T_N in the HP phase would be lower than T_N at $P = 0$ by a factor of 35/3. However, as the interatomic distance decreases, $I(0)$ grows. According to [3], the growth is linear, and $T_N \approx 600$ K in the vicinity of P_c (at $P = 0$, $T_N = 348$ K). With regard to the increase in the exchange interaction, we obtain the estimate $T_N \approx 50$ K for the HP phase. The electronic structure of a Mott–Hubbard insulator is characterized by the existence of local levels $\tilde{\Omega}_v = E_{1/2}(d^5) - E_1(d^4)$ (filled) and $\tilde{\Omega}_c = E_0(d^6) - E_{1/2}(d^5)$ (empty at $T = 0$) and by the dielectric ground state with the gap $E_g \sim U_{\text{eff}}$.

Thus, both considered variants lead to the conclusion that the HP phase is characterized by a dielectric antiferromagnetic ground state with the gap $E_g = 0.2$ eV. Both variants give values of T_N that are consistent with each other by the order of magnitude. The distinctions appear above T_N : the metal–insulator transition in the first variant and a semiconductor that transforms into a metal upon further buildup of the pressure, in the second variant. It is necessary to note that all quantitative estimates for the HP phase (for Δ_c , U_{eff} , and T_N values) should be considered as being qualitative, by the order of magnitude, rather than quantitative. Thus, the growth of the pressure will undoubtedly result in an increase in the uniaxial component of the crystal field, which will lead to further splitting of the e_g and t_{2g} states. Hence, the energies of all terms can change by a value comparable to Δ . Nevertheless, it is unlikely that the qualitative conclusion that U_{eff} significantly decreases upon the inversion of high-spin and low-spin terms will change if the model is refined. The conclusion that antiferromagnetism is retained in the HP phase, but with a lowered magnetic moment of the sublattice, was also obtained in [7]. In this work, the conclusion is drawn that the ground state is metallic at $P > P_c$. The interplay between the electrical and magnetic properties in the HP phase calls for further, primarily experimental investigation.

5. In conclusion, we note that the proposed model of the FeBO_3 band structure takes into account strong electron correlations and describes the optical absorption spectrum. The main mechanism of the change of the electronic structure with pressure is the increase in the crystal field, which leads to the inversion of high-spin and low-spin terms for the d^4 , d^5 , and d^6 configurations. An unusual mechanism of the transition from the strong correlation regime to the regime of weak correlation is revealed. This mechanism involves a decrease in the effective Hubbard parameter along with the usual growth of the band width.

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