

Experimental Observation of the Virtual Electronic States of a Mott–Hubbard Insulator FeBO₃ in Infrared Absorption Spectra

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A number of new peaks close to the previously predicted energies of virtual electronic states [S.G. Ovchinnikov and V.N. Zabluda, Zh. Eksp. Teor. Fiz. **125**, 150 (2004) [JETP **98**, 135 (2004)]] have been observed in the absorption spectra of FeBO₃ single crystals in the infrared range. The 0.27-eV peak was absent in the scheme presented in the work cited above and, to explain it, a multielectron theory taking into account the ²T₂ low-spin term of the Fe³⁺ ion has been developed.

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1. As is known, the standard band theory is inapplicable in systems with strong electron correlations. If strong electron correlations are consistently taken into account, the zeroth approximation in interatomic jumps of electrons involves a set of multielectron terms of the d^n configurations, and electrons are described as $d^n \rightarrow d^{n+1}$ excitation quasiparticles. Such an approach was proposed for the Hubbard model with the d^0 , d^1 , and d^2 configurations [1]; its development for the case of arbitrary configurations (generalized tight-binding (GTB) method) was described in [2]. In the general case, an electron is represented as a superposition of quasiparticles, Hubbard fermions, each corresponding to the creation of an electron ($d^n \rightarrow d^{n+1}$ excitation) or a hole ($d^n \rightarrow d^{n-1}$). Each configuration d^n has the main term and excited terms; their energies are calculated in the GTB method by the exact diagonalization of the Hamiltonian of one unit cell taking into account strong electron correlations. Quasiparticles are characterized by the energy $\Omega_{ij} = E_i(n+1) - E_j(n)$ and spectral weight $F_{ij} = N_i + N_j$, where N_j is the probability of the population of the multielectron term $E_j(d^n)$. The electronic structure of a substance is formed due primarily to quasiparticles with a nonzero spectral weight (excitations from the filled main term of the d^n configuration) similar to the states of the lower and upper Hubbard bands. The transitions between excited terms with zero spectral

width were revealed in the GTB calculations of La₂CuO₄ cuprates and were called virtual electronic states [3]. Similar virtual Hubbard fermions were obtained in [4, 5], where the electronic structures of FeBO₃ and VBO₃ were described using the multielectron GTB method, and in [6], where the electronic structure of Fe_{1-x}V_xBO₃ solid solutions was studied. In this work, we report the results of the first experimental observation of virtual electronic states in the infrared absorption spectra of FeBO₃ single crystals. Most of the observed features in the infrared spectra are close to the energies of virtual electrons predicted in [4, 6]. A peak that was absent in the density of states obtained in [4, 6] is detected. To explain it, a theory taking into account the ²T₂ low-spin term of the d^n configuration of the Fe³⁺ ion is developed.

2. The FeBO₃ single crystals were grown by the spontaneous crystallization method from a solution in a melt; the technology was described in detail in [7]. Crystals are thin (20–40-μm) green semitransparent hexagonal plates. The C₃ optical axis is perpendicular to the plate plane. The sample surface was not processed and polished before the measurements. The absorption and repulsion spectra were recorded on a high-sensitivity automated setup based on an IKS-21M prism spectrometer in the infrared range of 0.09–1.2 eV. A Globar and a serial bismuth bolometer were used as a radiation source and a detector, respectively.

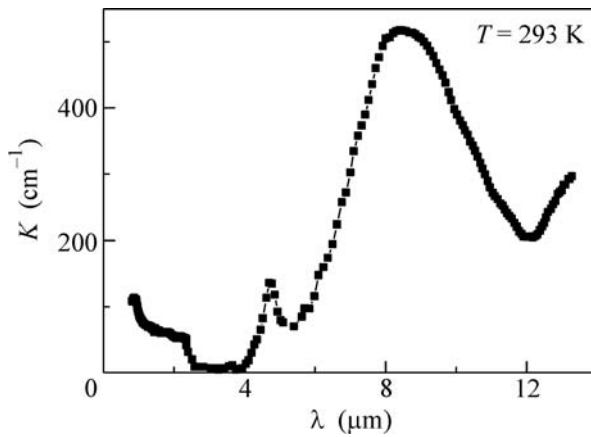


Fig. 1. Absorption spectrum of the FeBO₃ single crystal in the infrared range at room temperature.

For the measurements in a wide spectral range, we used a set of replaceable prisms made of NaCl, glass, and KRS-5. Light from the source was focused on the sample and directed perpendicularly to the plate plane.

A deep minimum characteristic of high-resistance semiconductors is observed in the reflection spectra below an intense phonon band at 7.83 μm (0.158 eV). The absorption spectra are more informative (see Fig. 1). In addition to an intense band at 8.37 μm (0.148 eV), a pronounced peak at 4.65 μm (0.27 eV) and a band at 1–2 μm are observed for FeBO₃ single crystals. The absorption coefficient is minimal near 3 μm . The shape of the absorption spectra at liquid-nitrogen temperature is similar. The existence of the absorption band in the transparency window of a semiconductor (in the band gap region) is experimental evidence of electronic transitions that were not previously observed for this compound.

3. Although the FeBO₃ crystal, which is transparent in the visible range and has spontaneous magnetization at room temperature, has long been investigated, it is still of interest. The optically induced quenching of the magnetic order under pulsed pumping [8], as well as the magnetic phase transition at a high pressure with the spin crossover of the Fe³⁺ ion from a high-spin state (⁶A₁) to a low-spin one (²T₂) [9], was recently detected in it. The electronic structure is formed by strong electron correlations inside the iron ion. According to single-electron band calculations, FeBO₃ is a metal [10]. The multielectron model of FeBO₃ based on the GTB method was proposed in [4, 11].

The first step in GTB calculations is the exact diagonalization of the Hamiltonian of one unit cell; in this case, one FeBO₃ formula unit is considered as a unit cell. As mentioned in [4, 11], the *p*–*d* hybridization of oxygen and iron is negligibly small; for this reason, the

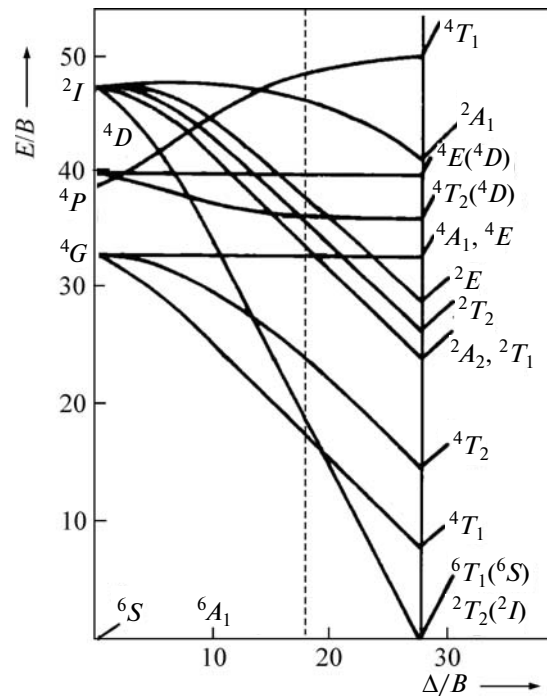


Fig. 2. Tanabe–Sugano scheme for the Fe³⁺ ion. The vertical straight line with $\Delta/B = 18.68$ gives the energies of the excited terms of FeBO₃ different from the main ⁶A₁ term (according to [16]).

first stage of the GTB calculation is reduced to the determination of the eigenstates of the *dⁿ* ion in a given crystal field. The Fe³⁺ ion in the stoichiometric FeBO₃ compound has a *d⁵* configuration. To describe the creation and annihilation of a *d* electron, it is necessary to know the terms of *d⁶* and *d⁴* configurations. The problem of determining the terms of the *dⁿ* configurations in a cubic crystal field (the deviation of the crystal field of FeBO₃ from cubic is small and we neglect it) has been solved long ago [12, 13]. We can use those calculations in which the energies of the terms are expressed in terms of the Racah parameters. The Racah parameters for FeBO₃ are taken from optical measurements.

The dielectric gap in FeBO₃ determines the optical absorption edge $E_{g0} = 2.9$ eV [14], which contains three bands (*A*, *B*, and *C*) of the *d*–*d* transitions. The Racah parameters $B = 680$ cm^{−1} (0.084 eV) and $C = 3160$ cm^{−1} (0.39 eV), as well as the cubic crystal field $\Delta = 12700$ cm^{−1} (1.57 eV), are determined from the optical and magneto-optical measurements. The Tanabe–Sugano scheme for the *d⁵* configuration and its section by a vertical line with $\Delta/B = 18.68$, which provides the values of various terms for FeBO₃, are shown in Fig. 2. The energies of these terms are

$$\begin{aligned} E_0 &= E(^6A_1), E(^4T_1) - E_0 = 1.39 \text{ eV}, \\ E(^2T_2) - E_0 &= 1.50 \text{ eV}, E(^4T_2) - E_0 = 2.03 \text{ eV}, \end{aligned} \quad (1)$$

$$E(^4A_1, ^4E) - E_0 = 2.80 \text{ eV.}$$

The first, third, and fourth excitations in Eqs. (1) are responsible for the $d-d$ transitions with $\Delta S = 1$ and form the A , B , and C peaks inside the dielectric gap. The excitations from the high-spin state (6A_1) to the low-spin one (2T_2) are doubly forbidden in spin and are not observed in usual absorption spectra.

The dielectric gap E_{g0} in FeBO_3 is formed by strongly hybridized s and p states of boron and oxygen in the BO_3 group. The contribution of the d electrons to the band structure is manifested primarily in the lower and upper Hubbard fermion bands. In this case, the energies of the lower and upper Hubbard bands are given by the expressions

$$\Omega_v = E(d^5, ^6A_1) - E(d^4, ^5E), \quad (2)$$

$$\Omega_c = E(d^6, ^5T_2) - E(d^5, ^6A_1), \quad (3)$$

respectively.

Since the Racah parameter A does not enter into the Tanabe–Sugano diagrams and is not determined in optical experiments, the value $\Omega_v = -1.4$ eV from the energy of a peak in the Fe L_α and O K_α X-ray emission spectra [10] was taken in [4] for the position of the Ω_v level with respect to the top of the valence band $\varepsilon_v = 0$. However, the accuracy of these methods is low: the energy resolutions are 2.5 and 0.5 eV for the first and second spectra, respectively [10]. For this reason, comparing the infrared spectra determined in this work, the optical spectra obtained in [15, 16], and the multielectron model of the electronic structure, the Ω_v level and the virtual levels of Hubbard fermions can be determined more accurately as compared to Fig. 3 in [4, 6]. Here, the virtual levels are determined as

$$\begin{aligned} \Omega'_v &= E(d^5, ^4T_1) - E(d^4, ^5E), \\ \Omega^* &= E(d^5, ^2T_2) - E(d^4, ^5E), \\ \Omega''_v &= E(d^5, ^4T_2) - E(d^4, ^5E), \\ \Omega'''_v &= E(d^5, ^4A_1) - E(d^4, ^5E). \end{aligned} \quad (4)$$

The spectral width for all of these excitations from an empty (unoccupied) state to another empty state is zero. Nevertheless, light can induce transitions from the top of the valence band to these states. In this case, the Ω'_v , Ω''_v , and Ω'''_v excitations in the infrared range have the same final states with the spin $S = 3/2$ as the A , B , and C peaks in the visible range and their energies are close to the values presented in Fig. 3 in [6]. Knowing the Ω'_v position from the infrared spectra (see Fig. 1), we obtain the more accurate position $\Omega_v =$

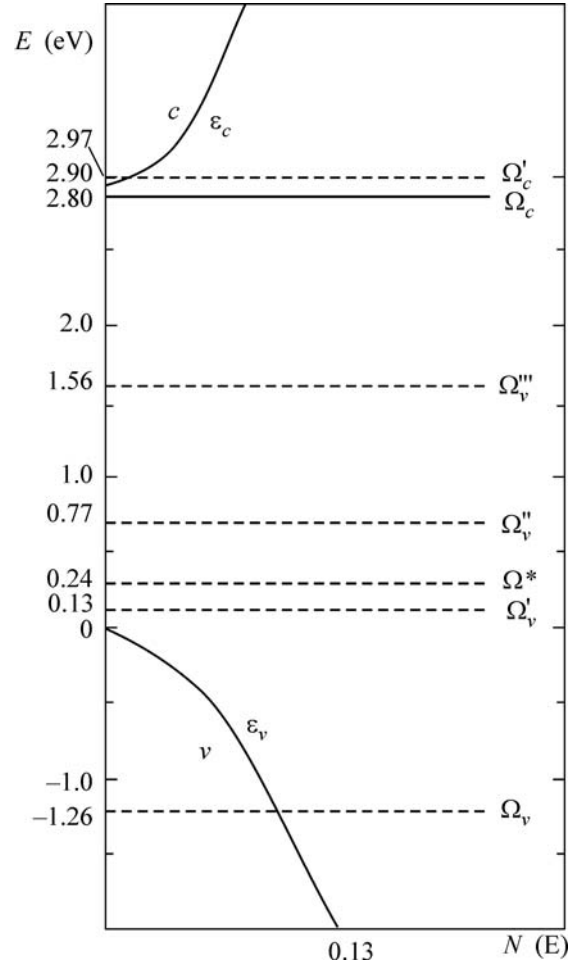


Fig. 3. Scheme of the density of states of FeBO_3 consistent with the infrared and visible spectra and with the Tanabe–Sugano scheme. The virtual levels and lower Hubbard band are shown by the dashed line and the upper Hubbard band is shown by the solid line.

-1.26 eV instead of -1.4 eV in [6]. Thus, the change is no larger than the errors of the X-ray emission spectra.

Figure 3 shows the scheme of the states of FeBO_3 that is refined as compared to [6]. The changes are generally small, but make it possible to coordinate the spectroscopic data in the infrared range, visible range, and Tanabe–Sugano diagram. The broadenings of the peaks in the density of states owing to the interatomic jumps are not shown in this scheme. The estimates of the parameters of a jump, which is suppressed by anti-ferromagnetic correlations of neighboring spins, give small widths of the d bands of about 0.1 eV [4]. Figure 4 shows $d-d$ excitons, as well as the fraction of fermions corresponding to the lower Hubbard band and virtual states.

The virtual quasiparticle Ω° requires particular attention, because the annihilation of an electron in the low-spin state 2T_2 in the d^5 ion can give only $S = 1$



Fig. 4. Scheme of the production of the excitons and fermions near the top of the valence band of FeBO₃. Excitons *A*, *B*, and *C* are shown by the vertical wavy lines, the lower band of Hubbard fermions is given by the solid line with arrows, and the virtual Hubbard fermions are shown by dashed lines.

in the d^4 ion. As a result, $\langle d^4, {}^5E|d|d^5, {}^2T_2 \rangle = 0$. However, the orbital angular momentum in the d^4 ion is partially unfrozen, $L = 1$. For this reason, the spin-orbit interaction forms the total angular momentum $J = 1, 2$, and 3 . The matrix element of the annihilation of an electron in the 2T_2 term of the d^5 configuration is nonzero for the d^4 term with $J = 1$. Thus, the virtual electronic level Ω^* with a finite low-spin term is observable in the infrared spectra. At the same time, excitons with the finite low-spin term are not observed in d^5-d^5 exciton excitations owing to double prohibition in spin.

4. It is worth noting that a number of peaks attributed to phonons with the A_{1g} and E_g modes, including the E_g mode with an energy of 1210 cm^{-1} (0.15 eV), were previously observed in the Raman spectra of FeBO₃ single crystals [17]. Therefore, from the commonly accepted point of view, the 0.15-eV peak in Fig. 1 would be associated with the E_g phonon. However, the analysis of the Raman spectra of three isostructural borates FeBO₃, VBO₃, and InBO₃ in Fig. 2 in [17] reveals an interesting feature: the frequencies of the A_{1g} and E_g modes are close to each other in all three crystals owing to the structural closeness. The intensities of identical modes in different crystals are also close to each other, except for the E_g mode with an energy of 1210 cm^{-1} (0.15 eV) for which the intensity in FeBO₃ is an order of magnitude higher than that in two other borates. The VBO₃ and InBO₃ borates have no virtual electronic states in this energy range, whereas the FeBO₃ borate has such states.

We think that the coincidence of the electron virtual excitation with the phonon energy increases the intensity by an order of magnitude. We decompose the intense 0.148-eV band in the absorption spectrum into two lines of Lorentzian shapes (see Fig. 5) with centers at 0.13 and 0.15 eV . The latter energy coincides with the 1210-cm^{-1} energy of the E_g phonon. The 0.13-eV line corresponds to the Ω_v electronic excitation.

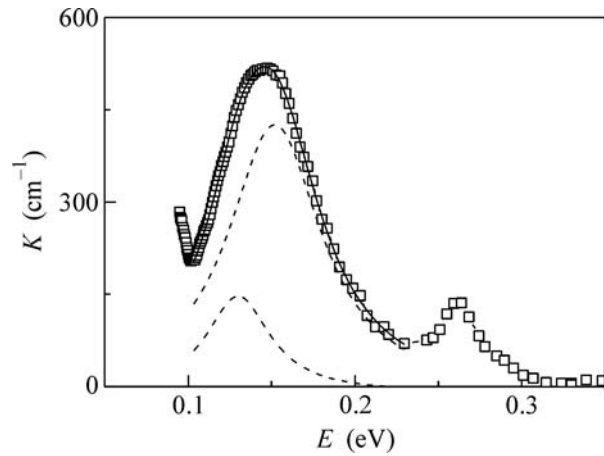


Fig. 5. Decomposition of the intense absorption band into two Lorentzian lines with energies of 0.15 ($1210\text{-cm}^{-1} E_g$ phonon) and 0.13 eV (Ω_v electronic excitation).

To conclude, we emphasize that the measured infrared spectra not only confirm the previously predicted virtual states of Hubbard fermions, but also stimulate the further development of the theory of the electronic structure of systems with strong electron correlations.

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