

Research Article

The $3d$ -electron states in FeBr_2 [♠]

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The fundamental controversy about the electronic structure for $3d$ -electron states in FeBr_2 is discussed. We advocate for the localized electron atomic-like many-electron crystal-field approach that yields the discrete energy spectrum, in the scale of 1 meV, associated with the atomic-like states of the Fe^{2+} ions in contrary to the (semi-)continuous energy spectrum provided by band theories. In our approach the six d electrons of the Fe^{2+} ion in FeBr_2 form the highly-correlated atomic-like electron system $3d^6$ described by two Hund's rules quantum numbers $S=2$ and $L=2$ with taking into account the spin-orbit coupling. The superiority of our model relies in the fact that it explains consistently properties of FeBr_2 , the insulating and the magnetic ground state as well as thermodynamics and Raman low-energy spectra, using well-established physical concepts.

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I. INTRODUCTION

There is a fundamental controversy in the description of $3d$ states in FeBr_2 . This controversy is related to the origin of the magnetism and of the electronic structure of $3d$ -atom containing compounds. The understanding of the magnetism and of the electronic structure is very closely related to a general problem "how to treat d electrons in $3d$ -atom containing compounds". The

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fundamental controversy "how to treat d electrons" starts already at the beginning - should they be treated as localized or itinerant (in the scientific physics sense, i.e. the localized or the itinerant picture should be taken as the start). Directly related to this problem is the structure of the available states: do they form the continuous energy spectrum like it is in the band picture or do they form the discrete energy spectrum typical for the localized states. Recently, at the beginning of 2002, Youn, Sahu and Kim (YSK) have presented an all-electron fully relativistic density-functional calculations, an extension of the density-functional approximation (LDA), for the electronic structure and the resulting magnetic moment, including the orbital moment [1]. This paper followed a paper of Ropka, Michalski and Radwanski (RMR), from May 2001, who have presented, within the quasi-atomic approach, the electronic structure and the resulting properties like spin and orbital contributions to the magnetic moment of the iron atom and thermodynamics [2]. YSK claim, contradicting the earlier RMR result for the spin-orbit coupling origin of the orbital moment, that the orbital moment is rather due to the strong on-site correlations of the $3d$ orbitals. The aim of this paper is to show up that both approaches largely concurs as far as the origin of the orbital moment is concerned. However, there is a fundamental difference between these two approaches as far as the description of the electronic structure and the physical nature of the $3d$ states is discussed. According to us, this fundamental difference in the electronic structure can be experimentally revealed and can be used as the experimental verification of different theoretical approaches.

II. THEORETICAL APPROACHES

The electronic structure for the $3d$ electrons in the YSK approach is related to the band description. Youn et al. have extended the standard local density approximation (LDA), in fact the LSDA, calculations by introducing a large intraorbital correlation energy U of the d electrons. Such the calculations are known as L(S)DA+ U calculations [3–7]. Their L(S)DA+ U results for the d -electron states, presented in Fig. 3c of Ref.[1], are schematically shown in Fig. 1. The energy spectrum for the $3d$ states contains continuous, though quite narrow, bands centered at -9.6, -8.9 and -6.8 eV (built up from 5 spin-up states) and at -0.2, +1.6 and +2.2 eV for the spin-down states. Thus, the occupied $3d$ states spread over ~ 10 eV. A gap, needed for the insulating state, within this band picture is obtained by the correlation energy U [1]. The general shape of the bands presented in Fig. 1 can be somehow understood knowing the localized states within the one-electron crystal field. The continuous energy spectrum looks like the smooth convolution on the available, largely spread, localized $3d$ one-electron orbitals, t_{2g} and higher e_g orbital. According to this picture 6 electrons (spins) of the Fe^{2+} ion are put subsequently one by one on the one-electron states formed for one d electron in the octahedral crystal field (CEF): three spins are put to the spin-up t_{2g} orbitals, other two occupies spin-up e_g orbitals, and the last sixth electron has to oc-

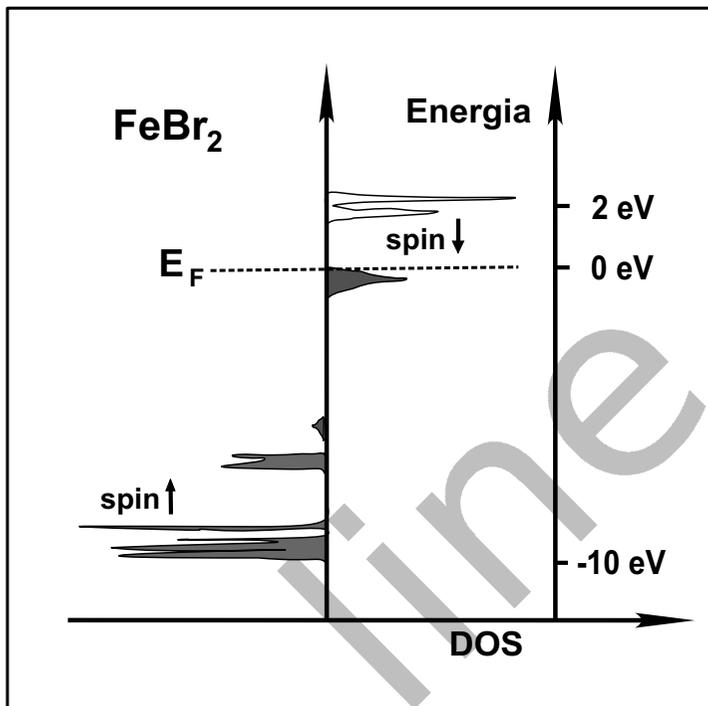


FIG. 1: Description of the d states in FeBr_2 within the band approach obtained within the $L(S)DA+U$ approach of Youn *et al*, Fig. 3c of Ref. [1]. There is a semi-continuous energy spectrum of the d states spread over 10 eV.

copy one spin-down t_{2g} orbital. According to Refs [1] such the electron/spin arrangement satisfies the first Hund's rule.

Ropka et al.'s description, Ref. [2], of the electronic structure, Fig. 2, is related to the localized picture, but with taking into account **two** Hund's rules and the intra-atomic spin-orbit coupling. In this atomic-like many-electron CEF approach the 6 d electrons in the open $3d$ shell form the highly-correlated intra-atomic $3d^6$ electron system. The strong correlations among the $3d$ electrons are accounted for, in a zero-order approximation, by two Hund's rules. The two Hund's rules yield for the d^6 system the ground term 5D with $S=2$ and $L=2$. Its 25-fold degeneracy is removed by the crystal field and spin-orbit interactions. In the octahedral bromium-anion surrounding of the Fe^{2+} ion, realized in the hexagonal structure of FeBr_2 , the orbital triplet ${}^5T_{2g}$ is lower than the orbital doublet 5E_g , being separated by Δ of about 2 eV. The T_{2g} ground subterm is confirmed by our *ab initio* calculations of the octupolar

potential (the A_4 CEF coefficient) at the Fe site in the bromium-anion octahedron. The A_4 CEF coefficient in the center of the anion octahedron is positive. The A_4 CEF coefficient together with the Stevens factor β for the $3d^6$ system, of $+2/63$ ([8], table 19 on page 873), yields the positive value of the octahedral CEF parameter B_4 and the ${}^5T_{2g}$ ground subterm. The positive sign for B_4 in the anion octahedron has been derived already a pretty long time ago by Abragam and Bleaney ([8], see page 374). However, this result has been completely forgotten, not saying about the ignorance of the crystal-field theory, in the current theoretical solid-state physics.

III. RESULTS AND DISCUSSION

In general, we take the VSK results as the confirmation of our result about the substantial orbital moment. We fully agree that the orbital moment is mostly due to the correlations of the $3d$ orbitals, though the YSK paper tries to contradict both our results about the origin of the large orbital magnetic moment pointing out that Ropka et al. have speculated (no, no, we have calculated it, and we can prove it!!!) that the orbital moment is due to the spin-orbit coupling. According to us, our statement about the spin-orbit coupling origin of the orbital moment does not exclude the correlation effects. In contrary, our many-electron CEF approach considers d electrons in the very strong correlation limit. It was, somehow, correctly recognized by VSK that in the quasi-atomic model the d - d on-site correlations are included inherently (by two Hund's rules and mainly by working in the many-electron basis), despite of their lack in the explicit form. The obtained value of the ordered magnetic moment at zero temperature amounts to $4.26 \mu_B$. It is built up from the spin moment of $+3.48 \mu_B$ and from the orbital moment of $+0.78 \mu_B$ [2]. We point out that the same sign of the spin and orbital moments comes out directly from our calculations and is related to the negative sign of the intra-atomic spin-orbit coupling. The effective moment calculated from the χ^{-1} vs T plot in the 300-400 K region, i.e. in the paramagnetic phase, amounts to $5.39 \mu_B$. It is only a slightly larger value than the spin-only value of $4.90 \mu_B$ what is a surprise owing to the fact that the full quantum orbital value $L (=2)$ is taken into calculations.

Our description of the electronic structure of FeBr_2 proceeds within the intermediate crystal-field regime in contrary to the current-literature view that prefers the strong crystal field regime in the description of $3d$ -atom compounds. According to our picture, the crystal field is intermediate in the sense that it is stronger than the spin-orbit coupling but it is relatively weak because it does not break the intra-atomic arrangement of electrons within the $3d$ shell, as is in the one-electron version of the crystal-field theory. It means, that we think that the intra-atomic structure of a paramagnetic atom largely perseveres even when this atom becomes the full part of a solid - on this basis we have developed a Quantum Atomistic Solid-State Theory (QUASST) for compounds containing open $3d$ -/ $4f$ -/ $5f$ -shell atoms [9, 10]. This weak

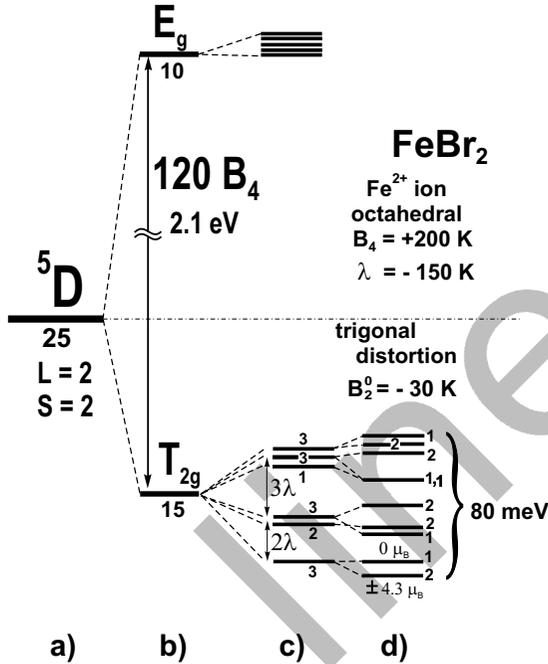


FIG. 2: The fine electronic structure of the highly-correlated atomic-like $3d^6$ electronic system of the Fe^{2+} ion in FeBr_2 . a) the 25-fold degenerated 5D term given by Hund's rules: $S=2$ and $L=2$. b) the effect of the octahedral crystal-field, c) the combined action of the spin-orbit coupling and the octahedral crystal field: $B_4=+200$ K, $\lambda=-150$ K; d) the electronic structure of the Fe^{2+} ion in FeBr_2 ; the trigonal-distortion parameter $B_2^0=-30$ K produces a spin-like gap of 2.8 meV; the double degeneracy of the ground state is removed in the magnetically-ordered state below T_N of 14 K. According to the Quantum Atomistic Solid State theory this fine structure is preserved in the solid FeBr_2 .

crystal-field approach, known within the rare-earth CEF community as the CEF approach, has been often successfully applied to $3d$ -ion doped systems, when $3d$ ions were introduced as impurities, in interpretation of, for instance, electron-paramagnetic-resonance experiments [8, 11, 12]. In Refs [13–16] we have applied this approach to a $3d$ -ion system where Co/Fe/Ni ions are the full part of a solid forming LaCoO_3 , FeO or NiO . Of course, in our picture the crystal field is much stronger than the spin-orbit coupling as is generally accepted in the $3d$ magnetism. It is worth noting that the CEF states in

our approach are many-electron states of the whole highly-correlated electron system $3d^6$. Moreover, in QUASST the magnetic state, below T_N of 14 K, is clearly distinguished from the paramagnetic state, see Fig. 4 of Ref.[2]. It is not clear how will look like the band electronic structure of Ref.[1] in the paramagnetic state, i.e. above T_N of 14 K, because it was not presented and not discussed in Ref.[1].

We would like to point out that the QUASST approach should not be considered as the treatment of an isolated ion - we consider the cation in the octahedral crystal field. This octahedral crystal field is predominantly associated with the anion octahedron FeBr_6 . The FeBr_2 structure is built up from the face sharing octahedra FeBr_6 - thus such the atomic structure occurs at each cation due to the translational symmetry. The strength of the crystal-field interactions is determined by the whole charge surroundings, not only by the nearest bromium octahedron. It makes that the CEF approach, in the version applied in QUASST, looks like a single-ion approach but in fact it describes the coherent states of the whole crystal. The parameters used in the discussion of properties of FeBr_2 in Ref. [2], are fully physical: the octahedral CEF parameter $B_4 = +200$ K, the trigonal $B_2^0 = -30$ K and the spin-orbit coupling $\lambda = -150$ K. They yield the overall effect of 2.06, 0.06, and 0.13 eV, respectively.

The electronic structure can be experimentally verified. In QUASST the shown states manifest in many physical properties like temperature dependence of the heat capacity, of the paramagnetic susceptibility χ , of the magnetic-moment value. The energy separations should be detected by energy spectroscopy experiments like Raman spectroscopy, for instance. In fact, we take old, but rather unknown, results of the Raman spectroscopy [17, 18] revealing a number of well-defined energy excitations as a confirmation of our atomistic model. The observed 8 excitations up to 637 cm^{-1} can be fully reproduced by our calculations with the same crystal-field parameters $B_4 = +200$ K and $B_2^0 = -30$ K and a spin-orbit coupling λ of -161 K: 0 (exp. - 0); 22.8 cm^{-1} (exp: -23 cm^{-1}); 181 (192); 209 (244); 281 (296); 516 (517); 517 (517); 608 (584); 630 (630); $636 (637 \text{ cm}^{-1})$ [19]. The fitted value for the spin-orbit coupling in FeBr_2 is only slightly larger than the assumed by us free-ion value of -150 K [20]. So good description of new type of experimental results with the parameters derived from analysis of the heat capacity and of the magnetic moment we take as a strong argument for the high physical adequacy of QUASST.

IV. CONCLUSIONS

In conclusion, we point out that the band L(S)DA description of FeBr_2 , completed by the U term, largely concurs to the localized many-electron CEF description in revealing the very strong electron correlations determining the orbital magnetic moment. These two approaches can, however, be easily distinguished, as the proposed electronic structures are completely different.

Also the nature of the $3d$ states is completely different. We are in favour of the localized electron atomic-like many-electron crystal-field approach that yields the discrete energy spectrum associated with the atomic-like states of the Fe^{2+} ions. The superiority of our model relies in the fact that it consistently describes both zero-temperature properties of FeBr_2 and thermodynamics and it makes use of the well-defined physical concepts. Our atomic-like approach provides in the very natural way the insulating ground state for FeBr_2 independently on the lattice distortions. The success of the LDA+U calculations of Youn et al. is related to the orientation of LDA calculations to the strong intra-atomic $d-d$ correlation limit. According to us, the LDA+U calculations have to largely reproduce **two** Hund's rules. We welcome the paper of Ref.[1]-it bridges somehow LDA calculations and CEF calculations. However, we would like to put attention that our electronic structure is determined within the meV energy scale what is about 5000 times smaller than the band width of Ref. [1] of 0.5 eV.

◆ This paper is in a form as submitted to Phys. Rev. B in June 2002. Later we have published another paper on FeBr_2 in Phys. Rev. B **63**, 172404 (2003). Ref. [9] has been now published in this volume.

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