Pis'ma v ZhETF, vol. 115, iss. 2, pp. 108 – 109

On the *ab initio* calculations within DFT + U approach of physical properties of a compound with strong electron-electron correlations by the case of $KFeS_2$

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Submitted 24 November 2021
Resubmitted 25 November 2021
Accepted 29 November 2021

DOI: 10.31857/S1234567822020070

A ternary potassium-iron sulfide, $KFeS_2$, belongs to a family of quasi-one-dimensional compounds with the general chemical composition $AFeCh_2$ (where A = K or Rb; Ch = S or Se) [1]. Nevertheless, so far, no consensus has been reached on the magnetic ground state of this compound. The correctness of an anticipated Spin-Hamiltonian and corresponding approximations to describe a certain magnetic sub-system of a compound can be checked by comparing the experimental magnetic specific-heat data with the theoretical predictions derived from the model [2]. The magnetic specific heat of a compound can be obtained as a difference between total specific heat and all the other contributions exclude the magnetic one [3].

One way to obtain the lattice specific heat is based on *ab initio* calculations. Density functional theory (DFT) calculations allow to obtain all the phonon modes of a crystal, while the lattice specific heat could be calculated from phonon density of states within the quasi-harmonic approximation [4, 5].

Nevertheless, in the case of a compound with strong electron-electron correlations, like $KFeS_2$ [6], approaches based on DFT calculations are not well applicable.

DFT + U approach greatly improves the description of materials with mixed type of electron distribution. This materials class includes mid-to-late first row transition metal oxides and sulfides, because the self-interaction error is largest for such multiply charged (i.e., +2 or higher) open-shell metal ions [7]. In the case of magnetically ordered compounds right choice of the U_{eff} parameter is necessary for the correct description of magnetic ground state and magnetic moments value [8]. The magnetic ground state and magnetic moment values of iron ions are well known from neutron diffraction measurements, below Neel temperature of 250 K [6] $KFeS_2$ is an antiferromagnet with the magnetic moments value 1.9 μ_B [1].

We have performed the series of *ab initio* calculations of the magnetic and electronic properties of $KFeS_2$ for the different U_{eff} parameter values. The *ab initio* calculations were based on DFT [9]. As a first approximation the calculations were performed implementing simplified LSDA + U approach [10] with a single parameter $U_{\mathrm{eff}} = U - J$ (the difference between Coulomb and exchange energies [11]).

The conformity between the calculated magnetic moment value and experimentally measured one were obtained for the negative parameter value U_{eff} ($U < J$) of -2 eV.

The correct description of magnetic properties of $KFeS_2$ within DFT + U approach with U_{eff} parameter value of -2 eV allows to assume that this model can be used for the correct prediction of all physical properties of the compound. Nevertheless, the predicted by the model electronic properties of $KFeS_2$ are in conflict with available experimental data [12].

Therefore, to obtain the agreement of *ab initio* and experimental results on both electronic and magnetic properties we have performed another series of calculations within the rotationally invariant LSDA + U approach proposed in [13]. On site Coulomb terms U and J have been considered independently for the strong correlated Fe d-electrons.

In a low temperature range $T < T_N \approx 250$ K, electrical resistivity of $KFeS_2$ exhibits exponential increasing [12]. Thus we used the intrinsic semiconductor model in order to describe experimental dependency. The best agreement have been obtained for the band gap value of $E_g \approx 0.35$ eV.

The dependency of calculated within DFT + U approach magnetic moment value on iron ions in $KFeS_2$ on chosen U and J parameters is presented on Fig. 1. The calculated magnetic moment value on iron ions in $KFeS_2$

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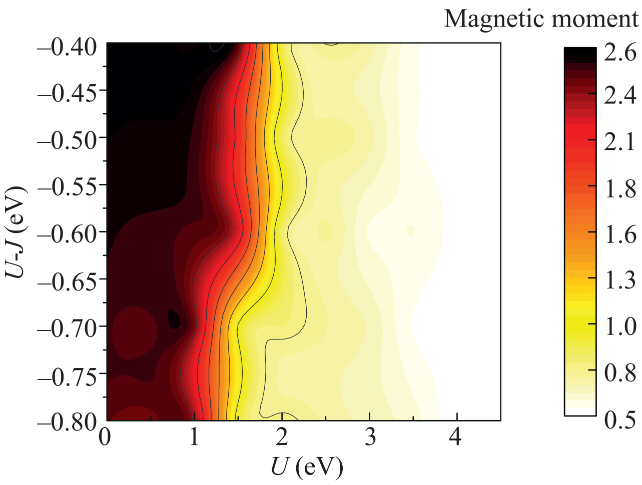

Fig. 1. (Color online) The calculated magnetic moment value on iron ions in $KFeS_2$ obtained for different values of U and J parameters

matches with experimental one (1.9 μ_B [1]) for the set of U and J parameters. The calculations give the correct value of magnetic moment for parameter J of approximately 2 eV and U in the range at least of 1.0–1.5 eV. So, in the case of calibration of U and J parameters by the correctness of magnetic moment values the particular pair of correct parameter values can not be proposed. The calculations within DFT + U approach with different combinations of U and J parameters can reproduce correct magnetic ground state and magnetic moment value while the predicted electronic properties are not in agreement with real properties. Finally, within the rotationally invariant DFT + U approach with $U = 1.5$ eV and $J = 2$ eV parameters, the magnetic and electronic properties of $KFeS_2$ are described correctly.

To summarize, the magnetic and electronic properties of iron chalcogenide compound $KFeS_2$ have been calculated within two DFT + U approaches based on (i) simplified LSDA + U approach [10] with a single parameter $U_{\text{eff}} = U - J$ (the difference between Coulomb and exchange energies [11]) and (ii) rotationally invariant LSDA + U approach proposed in [13]. The first model with parameter $U_{\text{eff}} = -2$ eV correctly describes magnetic ground state and magnetic moment value of the compound but incorrectly predicts the compound to be a metal, while below Neel temperature $KFeS_2$ is a semiconductor with band gap value 0.35 eV. The second approach with the pair of values of the parameters of $U = 1.5$ eV and $J = 2$ eV simultaneously give correct description of magnetic and electronic properties. The correct values of band gap and magnetic moment on iron ions have been obtained. Mentioned above U and J parameters values can be proposed for the correct description of physical properties of $KFeS_2$ within DFT + U approach.

This work was supported by the joint RFBR-DFG (Russian Foundation for Basic Research – Deutsche Forschungsgemeinschaft (German Research Foundation)) project # 19-52-12068 (RFBR) and # KR 2254/3-1 (DFG).

We thank Dr. Yury Lysogorskiy for fruitful and stimulated discussions.

This is an excerpt of the article "On the *ab initio* calculations within DFT + U approach of physical properties of a compound with strong electron-electron correlations by the case of $KFeS_2$". Full text of the paper is published in JETP Letters journal. DOI: 10.1134/S0021364022020023

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