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2009 J. Phys.: Condens. Matter 21 305501

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Electronic and magnetic structure for the spin-gapped system CuTe_2O_5

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Received 12 March 2009, in final form 11 June 2009

Published 6 July 2009

Online at stacks.iop.org/JPhysCM/21/305501

Abstract

The results of the calculation of the electronic and magnetic properties for the spin-gapped material CuTe_2O_5 are presented. The direct computation of exchange constants J in the framework of the LDA + U shows that the largest exchange coupling in CuTe_2O_5 is found between fourth nearest neighbors, as was argued by Das *et al* (2008 *Phys. Rev.* **77** 224437), and that this compound should be considered as the two-dimensional coupled dimer system.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The study of electronic and magnetic properties of low-dimensional magnets is an important and gradually growing field in condensed matter physics. One of the most interesting features in such systems is the development of the spin-gapped state [1]. For the simplest materials with structurally isolated dimers, the origin of such a state is trivial: a finite energy difference between ground and excited states. For others, like $\text{Ti}_2\text{Ru}_2\text{O}_7$, it is a consequence of an interplay between different degrees of freedom [2].

Recently the seemingly obvious origin of the spin-gap state, due to structurally formed lone pairs of Cu ions [3], in a low-dimensional material CuTe_2O_5 , was questioned in electron spin-resonance investigations (ESR) [4]. In order to explain the anisotropy and ESR linewidth the authors of [4] used an extended Huckel tight-binding method to study different exchange paths. In contrast to naive expectations the strongest exchange interaction was found to be between sixth nearest neighbor Cu ions (J_6) [4]. This interpretation was further questioned by the *ab initio* band structure investigation [5]. Based on the calculations of hopping parameters within the local density approximation (LDA) it was claimed that the strongest exchange interaction is expected to be between fourth nearest neighbors (J_4) [5]. Due to a large number of fitting parameters (exchange constants) both models can be equally well fitted to experimental susceptibility data.

In the present paper we performed a direct calculation of the exchange constants within the LDA + U approach and show that the strongest exchange interaction is between fourth

nearest neighbors and that CuTe_2O_5 should be considered as a two-dimensional coupled spin-dimer system. The calculations take into account strong Coulomb correlations on Cu, which leads to an insulating ground state. The electronic structure obtained in the present paper can be directly compared with results of spectroscopic studies.

2. Methods

In the present paper we used the structural and magnetic data obtained in [4] and [6]. The calculations were performed within the LDA and LDA+ U approximations in the framework of the linear muffin-tin orbitals method (LMTO) [7]. The Cu(4s, 4p, 3d), O(2s, 2p, 3d) and Te(5s, 5p, 5d) orbitals were included to the basis set. The MT sphere radii were taken to be 2.37 au, 2.42 au, and 1.7 au for Cu, Te, and O correspondingly. In our LMTO calculations we used the von Barth–Hedin exchange–correlation potential [8]. Since there is no certainty in the value of the on-site Coulomb repulsion parameter U for Cu in the literature [9–12], we carried out calculations for two representative and physical meaning values of U : 8 and 10 eV. Hund’s rule coupling (J_H) parameter was taken to be $J_H = 1$ eV. The Brillouin-zone (BZ) integration in the course of self-consistency iterations was performed over a mesh of 20 \mathbf{k} -points in the irreducible part of the BZ.

The exchange constants were computed for the Heisenberg Hamiltonian, which is written in the following form:

$$H = \sum_{ij} J_{ij} \vec{S}_i \vec{S}_j, \quad (1)$$

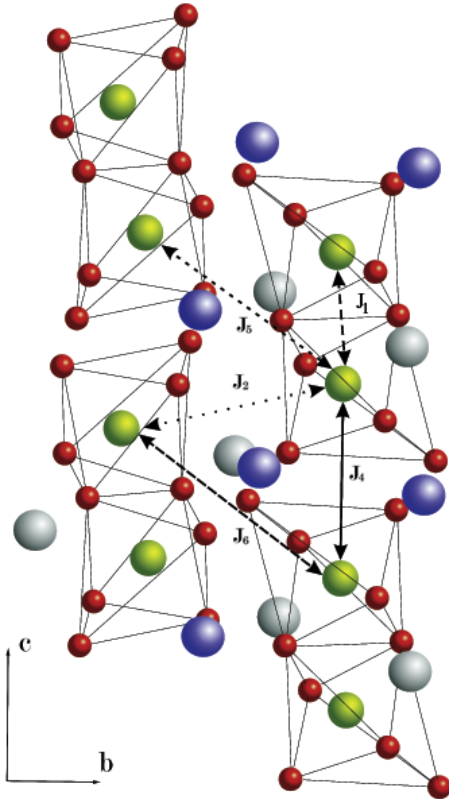


Figure 1. Crystal structure of CuTe_2O_5 . The projection on the bc -plane is shown. The largest gray and blue (dark grey in the printed edition) balls represent Te1 and Te2. Medium sized green balls are Cu ions located at the center of the distorted oxygen (shown as small red balls) octahedra. At the figure exchange integrals are marked. The a -axis points out of the plane of the figure (note that because of the monoclinic symmetry of CuTe_2O_5 this means that the plane shown in the figure does not coincide with the bc -plane).

where summation runs twice over every pair i, j . In order to compute exchange constants (J_{ij}) we utilized Lichtenstein's exchange interaction parameters (LEIP) calculation procedure, where one finds J as a second derivative of the energy with respect to a small spin rotation [13].

3. Crystal structure

CuTe_2O_5 has the monoclinic symmetry (space group $P21/c$) with lattice parameters $a = 6.871 \text{ \AA}$, $b = 9.322 \text{ \AA}$, $c = 7.602 \text{ \AA}$, and $\beta = 109.08^\circ$ [6]. The crystal structure of this compound is characterized by chain-like sets of Cu–Cu dimers running along the crystallographic c -axis (see figure 1). Each Cu is placed in a distorted octahedron with six inequivalent oxygens O1, O2, O3, O4, O5 and O5', which is elongated along the O2–O5' axis. Two octahedra forming a structural dimer have a joint edge O5–O5'. Te1 ions are disposed between structural dimers at a given Cu chain while Te2 ions are located between chains of dimers.

4. Results and discussion

In order to check our results, we first of all repeated calculations within the local density approximation (LDA)

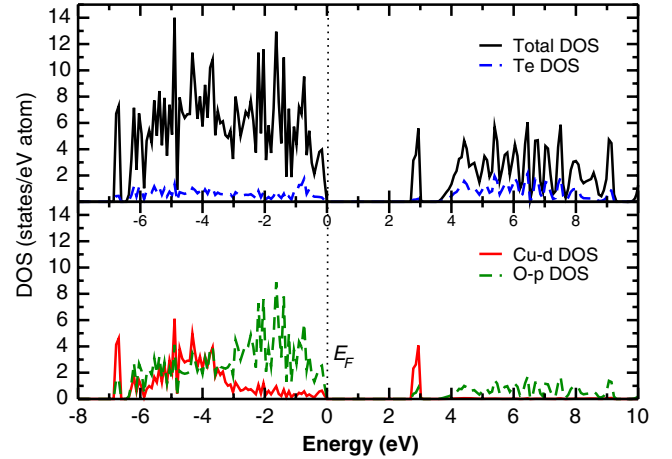


Figure 2. Total (solid black line) and partial (dashed blue and green lines for Te and O 2p states, solid red line for Cu 3d states) densities of states obtained in LDA + U calculations for $U = 8 \text{ eV}$. The Fermi energy is at zero.

Table 1. Cu–Cu distances (\AA) to the i th neighbor, hopping parameters t_i (meV) and their squared ratios.

i	Cu–Cu distance	t_i present work	$(t_i/t_4)^2$ present work
1	3.187	36.6	0.11
3	5.322	15.5	0.02
4	5.585	108.4	1.00
5	5.831	15.6	0.02
6	6.200	59.8	0.30
7	6.437	2.7	0.001

as was done in [5]. The Wannier projection technique was used to extract hopping parameters t_{ij} [14]. The results are summarized in table 1. One may see that they are essentially the same as those obtained in [5] using another method of calculation, but very different from the energy splitting parameters Δe found in [4].

The results of the hopping parameter calculations are related to exchange constants of the Heisenberg model via the well known $J = 2t^2/U$ formula in the simplest case of a pair of magnetic ions with the ferro-orbital type of ordering. In the real compounds low crystal symmetry and nontrivial orbital filling may lead to the deviation of J from the above mentioned relation [15, 16]. Therefore we performed the direct calculation of the exchange constants J . In order to take into account strong on-site Hubbard repulsion on Cu we employ the LDA + U approximation [17] for this purpose.

In contrast to the LDA [5], in the LDA + U approximation CuTe_2O_5 was found to be an insulator with the band gap 2.74 eV for $U = 8 \text{ eV}$ and 3.21 eV for $U = 10 \text{ eV}$. Corresponding DOSs are presented in figure 2. The conduction band is formed by hybridized O 2p and Te s, p states. The presence of a substantial hybridization makes exchange paths through Te and O especially effective.

The valence band is formed predominantly by Cu 3d states. The character analysis shows that it corresponds to x^2-y^2 orbitals. The elongation of the CuO_6 octahedron along

Table 2. Cu–Cu distances, leading exchange constants J_i obtained within LDA + U calculation and those recalculated from hoppings via $2t^2/U$, J_i/J_4 ratios for $U = 8$ and 10 eV. Note that proposed ratios of the exchange constants given in [5], $J_1/J_4 = 0.27$, $J_6/J_4 = 0.07$, are quite close to the values obtained in our direct calculations.

i	Cu–Cu dist. (Å)	$U = 8$ eV				$U = 10$ eV			
		J_i (LDA + U) (K)	$2t_i^2/U$ (K)	$2t_i^2/(UM_s^2)$ (K)	J_i/J_4	J_i (LDA + U) (K)	$2t_i^2/(UM_s^2)$ (K)	J_i/J_4	
1	3.187	5	4	6	0.08	3	4.5	0.08	
4	5.585	64	34	55	1.00	43	40.4	1.00	
6	6.200	19	10	17	0.30	13	12.3	0.31	

a local z direction leads to the crystal field splitting of the e_g shell. As a result the x^2-y^2 orbital goes up in energy and strong Coulomb repulsion stabilizes a hole on it. The spin magnetic moment on Cu ions was found to be $0.79 \mu_B$ for $U = 8$ eV and $0.82 \mu_B$ for $U = 10$ eV, which deviates from unity due to a substantial hybridization between Cu e_g and O $2p$ states.

In order to get exchange constants directly from the LDA + U calculation we constructed a supercell with $a' = a - c$, $b' = -(b + c)$, $c' = b - (a + c)$. Magnetic ordering of Cu ions in the supercell was taken accordingly in order to get AFM-type exchange constants J_1 , J_4 and J_6 . The results are summarized in table 2. The strongest exchange is between fourth nearest neighbors (J_4). Since J_4 is at least three times larger than any other exchange, one may consider CuTe₂O₅ as a two-dimensional coupled dimer system, where geometrical dimers do not coincide with magnetic ones.

One may see (from the third and fourth columns of table 2) that the J_i calculated within the LEIP procedure are in qualitative agreement with those recalculated from the hopping parameter via⁴ $2t^2/U$ as was proposed in [5]. Quantitative agreement may be achieved if one takes into account the fact that the hopping parameters were calculated in the Wannier function basis set, which is different from purely atomic d wavefunctions (in our case 3d LMT orbitals of Cu) used in the LEIP algorithm. The square of the contribution of other (mainly O $2p$) orbitals to the Wannier functions is proportional to the spin moment in LDA + U calculation. As a result the exchange constants should be calculated as $J \sim 2t^2/(UM_s^2)$, where M_s is the spin moment in the LDA + U calculation [18]. In other words, in the LDA + U we are calculating exchange constants not for the normal Heisenberg model with integer or half-integer values of the spins, but for the band problem where due to a substantial hybridization actual moments are much smaller. Thus, the factor of M_s^2 appearing in the denominator for the expression for J in equation (22) of [18] may be considered as due to an appropriate redefinition of the Heisenberg model. The exchange constants recalculated from the hoppings in this way are presented in the fifth and eighth columns of table 2.

In order to check the adequacy of the proposed coupled spin-dimer model for the description of magnetic properties of CuTe₂O₅ the computations of the magnetic susceptibility in the framework of the stochastic series expansion method were performed in [5]. It was shown that the best agreement with experimental results can be obtained for the coupling ratios $\alpha_1 = J_6/J_4 = 0.27$ and $\alpha_2 = J_1/J_4 = 0.07$. The exchange

constants obtained in the present work are very close to these estimates, being $\alpha_1 = 0.30$ and $\alpha_2 = J_1/J_4 = 0.08$ for $U = 8$ eV (for $U = 10$ eV, $\alpha_1 = 0.31$).

In the mean-field approximation one may also recalculate the Curie–Weiss temperature using exchange integrals as

$$\theta = \rho_S \sum_k z_k J_k \quad (2)$$

where $\rho_S = \frac{2}{3}S(S + 1)$ is the weight factor (for $S = \frac{1}{2}$, $\rho_S = \frac{1}{2}$) and z_k the number of exchange integrals J_k for Cu²⁺ ions in the CuTe₂O₅ compound (table 2). For the exchange constants listed in table 2, $\theta = 54$ K for $U = 8$ eV and $\theta = 36$ K for $U = 10$ eV, both in good agreement with the experimental Curie–Weiss temperature $\theta_{\text{exp}} = 41$ K in [4]. However, since the Curie–Weiss temperature calculated within mean-field theory is generally expected to overestimate the experimental value [19], the θ (and correspondingly the exchange constants) obtained for $U = 8$ eV seems more reasonable.

To sum up, in the present paper we performed a direct calculation of exchange constants within the LDA + U approximation and confirm that CuTe₂O₅ should be considered as a system of coupled spin-dimers, which do not coincide with geometrically closest pairs of magnetic ions.

Acknowledgments

We thank V Mazurenko for fruitful discussions. This work is supported by the Dynasty Foundation and the International Center for Fundamental Physics in Moscow, the Russian Foundation for Basic Research through RFFI 07-02-00041, German–Russian project 436 RUS 113/942/0, European research network SOPRANO, and the Civil Research and Development Foundation together with the Russian Ministry of Science and Education through grant Y4-P-05-15.

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⁴ Note that in contrast to [5] each pair of spins enters twice in the Heisenberg model and hence $J = 2t^2/U$, not $4t^2/U$ as in [5].

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