Structural Relaxation due to Electronic Correlations in the Paramagnetic Insulator $KCuF_3$

I. Leonov,[1] N. Binggeli,[1,2] Dm. Korotin,[3] V. I. Anisimov,[3] N. Stojić,[4,2] and D. Vollhardt[5]

[1]*Abdus Salam International Center for Theoretical Physics, Trieste 34014, Italy*
[2]*INFM-CNR Democritos, Theory @ Elettra group, Trieste 34014, Italy*
[3]*Institute of Metal Physics, South Kovalevskoy Street 18, 620219 Yekaterinburg GSP-170, Russia*
[4]*International School for Advanced Studies, SISSA, Via Beirut 2/4, 34014 Trieste, Italy*
[5]*Theoretical Physics III, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, Augsburg 86135, Germany*
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A computational scheme for the investigation of complex materials with strongly interacting electrons is formulated which is able to treat atomic displacements, and hence structural relaxation, caused by electronic correlations. It combines *ab initio* band structure and dynamical mean-field theory and is implemented in terms of plane-wave pseudopotentials. The equilibrium Jahn-Teller distortion and antiferro-orbital order found for paramagnetic $KCuF_3$ agree well with experiment.

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In materials with correlated electrons, the interaction between spin, charge, orbital, and lattice degrees of freedom leads to a wealth of ordering phenomena and complex phases [1]. The diverse properties of such systems and their great sensitivity with respect to changes of external parameters such as temperature, pressure, magnetic field, or doping also make them highly attractive for technological applications [1]. In particular, orbital degeneracy is an important and often inevitable cause for this complexity [2]. A fascinating example is the cooperative Jahn-Teller (JT) effect—the spontaneous lifting of the degeneracy of an orbital state—leading to an occupation of particular orbitals (“orbital ordering”) and, simultaneously, to a structural relaxation with symmetry reduction.

The electronic structure of materials can often be described quite accurately by density functional theory in the local density approximation (LDA) [3] or the generalized gradient approximation (GGA) [4,5]. However, these methods usually fail to predict the correct electronic and structural properties of materials where electronic correlations play a role. Extensions of LDA, e.g., LDA + U [6] and self-interaction correction LDA [7], can improve the results, e.g., the band gap value and local moment, but only for solids with long-range order. Hence the computation of electronic, magnetic, and structural properties of strongly correlated *paramagnetic* materials remains a great challenge. Here the recently developed combination of band-structure approaches and dynamical mean-field theory [8], the so-called LDA + DMFT computational scheme [9], has become a powerful new tool for the investigation of strongly correlated compounds in both their paramagnetic and magnetically ordered states. This technique has recently provided important insights into the properties of correlated electron materials [10], especially in the vicinity of a Mott metal-insulator transition as encountered in transition metal oxides [1].

Applications of LDA + DMFT so far mainly employed linearized and higher-order muffin-tin orbital [L(N)MTO] methods [11] and concentrated on the study of correlation effects within the electronic system for a given ionic lattice. On the other hand, the interaction of the electrons with the ions also affects the lattice structure. LDA + DMFT investigations of particularly drastic examples, the volume collapse in paramagnetic Ce [12,13] and Pu [14] and the magnetic moment collapse in MnO [15], incorporated the lattice by calculating the total energy of the correlated material as a function of the atomic volume. However, for investigations going beyond equilibrium volume calculations, e.g., of the cooperative JT effect and other subtle structural relaxation effects, the L(N)MTO method is not suitable since it cannot determine atomic displacements reliably. This is partly due to the fact that the atomic-sphere approximation used in the L(N)MTO scheme, with a spherical potential inside the atomic sphere, completely neglects multipole contributions to the electrostatic energy originating from the distorted charge density distribution around the atoms. By contrast, the plane-wave pseudopotential approach employed here does not neglect such contributions and can thus fully describe the effect of the distortion on the electrostatic energy.

In this Letter, we present a computational scheme which allows us to calculate lattice relaxation effects caused by electronic correlations. To this end, the GGA + DMFT—a merger of the GGA and DMFT—is formulated within a plane-wave pseudopotential approach [16–18]. Thereby the limitations of the L(N)MTO scheme in the direct calculation of total energies are overcome. In particular, we apply this new method to determine the orbital order and the cooperative JT distortion in the paramagnetic phase of the prototypical JT system $KCuF_3$.

$KCuF_3$ has long been known to be a prototypical material with a cooperative JT distortion [2] where the electronic degrees of freedom are the driving force behind the orbital order [2,6,19]. Indeed, the relatively high (tetragonal) symmetry makes $KCuF_3$ one of the simplest systems to study. In particular, only a single internal structure parameter, the shift of the in-plane fluorine atom from the Cu-Cu bond center, is needed to describe the lattice distortion. Moreover, there is only a single hole in the d shell so that complications due to multiplet effects do not arise. $KCuF_3$ is an insulating pseudocubic perovskite whose structure is related to that of high-T_c superconductors and colossal magnetoresistance manganites. The copper ions have octahedral fluorine surrounding and are nominally in a Cu^{2+} ($3d^9$) electronic configuration, with completely filled t_{2g} orbitals and a single hole in the e_g states. The cubic degeneracy of the Cu e_g states is lifted due to a cooperative JT distortion leading to an elongation of the CuF_6 octahedra along the a and b axes and an antiferro-distortive pattern in the ab plane [20]. This is associated with an alternating occupation of $d_{x^2-z^2}$ and $d_{y^2-z^2}$ hole orbitals along the a and b axes, resulting in a tetragonal compression ($c/a < 1$) of the unit cell. Purely electronic effects such as in the Kugel-Khomskii theory [2] and the electron-lattice [21] interaction have been discussed as a possible mechanism behind the orbital ordering in $KCuF_3$. The antiferro (a-type) and ferrolike (d-type) stacking of the ab planes along the c axis give rise to two different structural polytypes, which have been identified experimentally at room temperature [22].

Below the Néel temperature ($T_N \sim 38$ K for a-type and $\sim$22 K for d-type ordering), which is much lower than the critical temperature for orbital ordering, $KCuF_3$ shows A-type antiferromagnetic order [23]. The antiferromagnetic structure is consistent with the Goodenough-Kanamori-Anderson rules for a superexchange interaction with $d_{x^2-z^2}/d_{y^2-z^2}$ antiferro-orbital ordering. This is also found within LDA + U, which finds the correct orbitally ordered, antiferromagnetic insulating ground state [6,24], while the LDA predicts *metallic* behavior. Moreover, LDA + U calculations for a model structure of $KCuF_3$ in which cooperative JT distortions are completely neglected reproduce the correct orbital order, suggesting an electronic origin of the ordering [6,19] in agreement with the Kugel-Khomskii theory [2]. Altogether, LDA + U is able to determine the JT distortion in $KCuF_3$ rather well [6,24] but simultaneously predicts an additional long-range magnetic order. Therefore, LDA + U cannot explain the properties at temperatures above T_N and, in particular, at room temperature, where $KCuF_3$ is a correlated paramagnetic insulator with a robust JT distortion which persists up to the melting temperature. To determine the correct orbital order and cooperative JT distortion for a correlated paramagnet, i.e., to perform a structural optimization, we here employ GGA + DMFT.

We first calculate the GGA band structure of $KCuF_3$ at room temperature (space group $I4/mcm$) [20], employing the plane-wave pseudopotential approach [17,25]. Calculations are performed for values of the in-plane JT distortion δ_{JT} [26] ranging from 0.2% to 7% while keeping the lattice parameters a and c and the space group symmetry fixed. In the paramagnetic phase, and for all values of δ_{JT} considered here, the GGA yields a *metallic* rather than the experimentally observed insulating behavior, with an appreciable orbital polarization due to the crystal field splitting. Overall, the GGA results qualitatively agree with previous band-structure calculations [6,24]. Obviously, a JT distortion by itself, without the inclusion of electronic correlations in the paramagnetic phase, cannot explain the experimentally observed orbitally ordered *insulating* state of $KCuF_3$.

To include the electronic correlations, we construct an effective low-energy Hamiltonian $\hat{H}_{GGA}$ for the partially filled Cu e_g orbitals for each value of the distortion δ_{JT} considered here. This is achieved by employing the pseudopotential plane-wave GGA results and making a projection onto atomic-centered symmetry-constrained Cu e_g Wannier orbitals [16]. Taking the local Coulomb repulsion U and Hund's rule exchange J into account, one obtains the following low-energy Hamiltonian for the two ($m = 1, 2$) Cu e_g bands:

$$\hat{H} = \hat{H}_{GGA} + U\sum_{im} n_{im\uparrow}n_{im\downarrow} + \sum_{i\sigma\sigma'}(V - \delta_{\sigma\sigma'}J)n_{i1\sigma}n_{i2\sigma'} - \hat{H}_{DC}. \quad (1)$$

Here the second and third terms on the right-hand side describe the local Coulomb interaction between Cu e_g electrons in the same and in different orbitals, respectively, with $V = U - 2J$, and $\hat{H}_{DC}$ is a double-counting correction which accounts for the electronic interactions already described by the GGA (see below). To compute the electronic correlation-induced structural relaxation of $KCuF_3$, we calculate the total energy as [13,18]

$$E = E_{GGA}[\rho] + \langle H_{GGA}\rangle - \sum_{m,k}\epsilon_{m,k}^{GGA} + \langle H_U\rangle - E_{DC}, \quad (2)$$

where $E_{GGA}[\rho]$ is the total energy obtained by GGA. The third term on the right-hand side of Eq. (2) is the sum of the GGA Cu e_g valence-state eigenvalues and is given by the thermal average of the GGA Hamiltonian with the GGA Green function $G_{\mathbf{k}}^{GGA}(i\omega_n)$:

$$\sum_{m,k}\epsilon_{m,k}^{GGA} = \frac{1}{\beta}\sum_{n,\mathbf{k}}\mathrm{Tr}[H_{GGA}(\mathbf{k})G_{\mathbf{k}}^{GGA}(i\omega_n)]e^{i\omega_n 0^+}. \quad (3)$$

$\langle H_{GGA}\rangle$ is evaluated similarly but with the full Green function including the self-energy. The interaction energy $\langle H_U\rangle$ is computed from the double occupancy matrix. The double-counting correction $E_{DC} = \frac{1}{2}UN_{e_g}(N_{e_g} - 1) - \frac{1}{4}JN_{e_g}(N_{e_g} - 2)$ corresponds to the average Coulomb re-

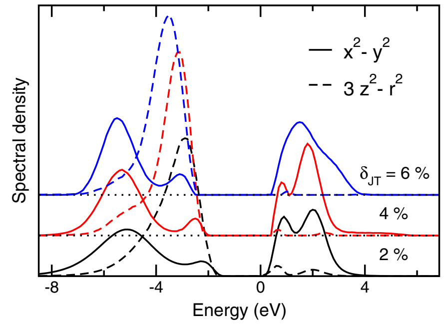

FIG. 1 (color online). Orbitally resolved Cu e_g spectral densities of paramagnetic $KCuF_3$ as obtained by GGA + DMFT(QMC) for different values of the JT distortion.

pulsion between the N_{e_g} electrons in the Cu e_g Wannier orbitals.

The many-body Hamiltonian (1) is solved within DMFT for $U = 7$ eV and $J = 0.9$ eV [6] using quantum Monte Carlo (QMC) calculations [27–29]. Figure 1 shows the spectral density of paramagnetic $KCuF_3$, obtained from the QMC data by the maximum entropy method, for three values of the JT distortion δ_{JT}. Most importantly, a paramagnetic insulating state with a strong orbital polarization is obtained for all δ_{JT}. The energy gap is in the range 1.5–3.5 eV and increases with increasing δ_{JT}. The sharp feature in the spectral density at about -3 eV corresponds to the fully occupied $3z^2 - r^2$ orbital [30], whereas the lower and upper Hubbard bands are predominantly of $x^2 - y^2$ character and are located at -5.5 and 1.8 eV, respectively.

The total energies as a function of the JT distortion obtained by the GGA and GGA + DMFT, respectively, are compared in Fig. 2. We note that the GGA not only predicts a *metallic* solution, but its total energy is seen to be almost constant for $0 < \delta_{JT} \lesssim 4\%$. Both features are in contradiction to experiment since the extremely shallow minimum at $\delta_{JT} \simeq 2.5\%$ would imply that $KCuF_3$ has no JT distortion for $T \gtrsim 100$ K. By contrast, the inclusion of the electronic correlations among the partially filled Cu e_g states in the GGA + DMFT approach leads to a very substantial lowering of the total energy by ~175 meV per formula unit. This implies that the strong JT distortion persists up to the melting temperature (>1000 K), in agreement with experiment. The minimum of the GGA + DMFT total energy is located at the value $\delta_{JT} = 4.2\%$, which is also in excellent agreement with the experimental value of 4.4% [20]. This clearly shows that the JT distortion in paramagnetic $KCuF_3$ is caused by electronic correlations.

An analysis of the occupation matrices for the e_g Cu Wannier states obtained by the GGA + DMFT calculations confirms a substantial orbital polarization in the calculated paramagnetic phase of $KCuF_3$. As shown in Fig. 3, the orbital order parameter (defined as the difference between $3z^2 - r^2$ and $x^2 - y^2$ Cu e_g Wannier occupancies [30]) saturates at about 98% for $\delta_{JT} \gtrsim 4\%$. Thus, the GGA + DMFT result shows a predominant occupation of the Cu $3z^2 - r^2$ orbitals. We note that, even without a JT distortion, the orbital order parameter would remain quite large (~40%). Moreover, while the GGA result for $\delta_{JT} = 0$ yields a symmetric orbital polarization with respect to C_4 rotations around the c axis, spontaneous antiferro-orbital order is found in GGA + DMFT. This difference is illustrated in Fig. 3, where insets (a) and (c) depict the hole orbital order obtained by the GGA and GGA + DMFT for $\delta_{JT} = 0.2\%$, respectively. The GGA charge density is more or less the same along the a and b axis [inset (a)]; i.e., the Cu $d_{x^2-z^2}$ and $d_{y^2-z^2}$ hole orbitals are almost equally occupied and hence are not ordered. By contrast, the GGA + DMFT results clearly show an alternating occupation [inset (c)], corresponding to the occupation of a $x^2 - y^2$ hole orbital in the local coordinate system, which implies antiferro-orbital order. For the experimentally observed value of the JT distortions of $\delta_{JT} = 4.4\%$, both the GGA and GGA + DMFT find antiferro-orbital order [insets (b) and (d)]. However, we note again that, in con-

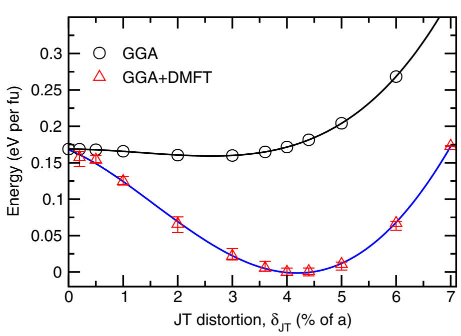

FIG. 2 (color online). Comparison of the total energies of paramagnetic $KCuF_3$ computed by the GGA and GGA + DMFT(QMC) as a function of the JT distortion. Error bars indicate the statistical error of the DMFT(QMC) calculations.

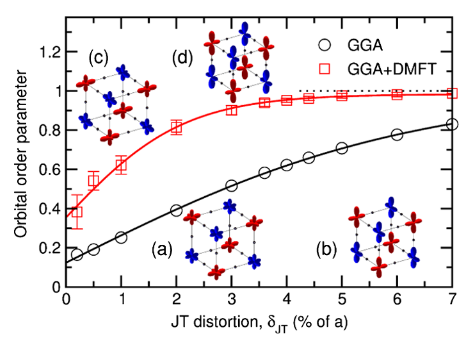

FIG. 3 (color online). Dependence of the orbital order parameter in paramagnetic $KCuF_3$ on the JT distortion as obtained by the GGA and GGA + DMFT(QMC), respectively. Error bars indicate the statistical error of the DMFT(QMC) calculations. Insets (a) and (b) refer to the GGA and (c) and (d) to GGA + DMFT results and show the hole orbital ordering for $\delta_{JT} = 0.2\%$ and 4.4% (see text).

trast to the GGA + DMFT, the GGA yields a *metallic* solution without any JT distortion for $T \gtrsim 100$ K, in contradiction to experiment.

In conclusion, by formulating GGA + DMFT—the combination of the *ab initio* band-structure calculation technique GGA with the dynamical mean-field theory—in terms of plane-wave pseudopotentials [16], we constructed a robust computational scheme for the investigation of complex materials with strong electronic interactions. Most importantly, this framework is able to determine the correlation-induced structural relaxation of a solid. Results obtained for paramagnetic $KCuF_3$, namely, an equilibrium Jahn-Teller distortion of 4.2% and antiferro-orbital ordering, agree well with experiment. The electronic correlations were also found to be responsible for a considerable enhancement of the orbital polarization. The GGA + DMFT scheme presented in this Letter opens the way for fully microscopic investigations of the structural properties of strongly correlated electron materials such as lattice instabilities observed at correlation-induced metal-insulator transitions.

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[25] Calculations were performed with the Perdew-Burke-Ernzerhof exchange-correlation functional [4] together with Vanderbilt ultrasoft pseudopotentials for Cu and F, a soft Troullier-Martin pseudopotential for K, and a kinetic energy cutoff of 75 Ry for the plane-wave expansion of the electronic states.
[26] We define the Jahn-Teller distortion by $\delta_{JT} = \frac{1}{2} \times (d_l - d_s)/(d_l + d_s)$. Here d_l and d_s denote the long and short Cu-F bond distances, respectively. The structural data [20] at room temperature yield $\delta_{JT} = 4.4\%$ (in units of the lattice constant a).
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[29] To simplify the computation, we neglected the orbital off-diagonal elements of the local Green function by applying an additional transformation into the local basis set with a diagonal density matrix during each DMFT iteration.
[30] The local coordinate system is chosen with the z direction defined along the longest Cu-F bond of the CuF_6 octahedron.