Effect of correlations and doping on the spin susceptibility of iron pnictides: the case of KFe$_2$As$_2$

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The temperature dependence of the paramagnetic susceptibility of the iron pnictide superconductor KFe$_2$As$_2$ and its connection with the spectral properties of that material is investigated by a combination of density functional theory (DFT) in the local density approximation and dynamical mean-field theory (DMFT). Unlike other iron pnictide parent compounds where the typical oxidation state of iron is 2, the formal valence of Fe in KFe$_2$As$_2$ is 2.5, corresponding to an effective doping with 0.5 hole per iron atom compared to, for example, BaFe$_2$As$_2$. This shifts the chemical potential and thereby reduces the distance between the peaks in the spectral functions of KFe$_2$As$_2$ and the Fermi energy as compared to BaFe$_2$As$_2$. The shift, which is clearly seen on the level of DFT as well as in DMFT, is further enhanced by the strong electronic correlations in KFe$_2$As$_2$. In BaFe$_2$As$_2$ the presence of these peaks results [Phys. Rev. B 86, 125124 (2012)] in a temperature increase of the susceptibility up to a maximum at $\sim$1000 K. While the temperature increase was observed experimentally the decrease at even higher temperatures is outside the range of experimental observability. We predict that in KFe$_2$As$_2$ the situation is different. Namely, the reduction of the distance between the peaks and the Fermi level due to doping is expected to shift the maximum in the susceptibility to much lower temperatures, such that the decrease of the susceptibility should become visible in experiment.

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I. INTRODUCTION

The discovery of high-temperature superconductivity in fluoride-doped LaFeAsO in 2008 by Kamihara et al. has placed the iron-arsenic systems into the center of activity of solid state physics. To date a variety of Fe-based superconductors have been found. The so-called '122' family (compounds with the common formula $\text{AFe}_2\text{As}_2$, where A=alkaline earth element) is the most studied one. Unlike other iron-arsenic systems, undoped compounds of the '122' family superconduct under pressure, with $T_c$ up to 29 K. The highest critical temperature, $T_c = 38$ K, in this family is detected in the potassium doped compound Ba$_{1-x}$K$_x$Fe$_2$As$_2$ with $x = 0.14$. Therefore KFe$_2$As$_2$ is the end member of the family and can be considered a parent compound in which superconductivity emerges under chemical doping. Although the critical temperature is rather low in KFe$_2$As$_2$ ($T_c$=3.8 K) this material is a rare example of a stoichiometric pnictide superconductor.

It is widely accepted that Coulomb correlations are crucial for the understanding of many aspects of the physics of pnictides. Correlation effects in KFe$_2$As$_2$ were intensively studied: Terashima et al. performed de Haas-van Alphen measurements of the Fermi surface in KFe$_2$As$_2$. They detected unusually large effective mass renormalizations and big differences in the masses of different bands, which is not found in other pnictides. The enhancement of the band mass was also measured by Yoshida et al. in angular-resolved photoemission spectroscopy (ARPES) experiments. Hardy et al. employed the Gutzwiller slave-boson mean-field method to study the strength of Coulomb correlations in KFe$_2$As$_2$. They confirmed the experimental conclusions of Terashima et al. and Yoshida et al., and proposed an orbital-selective scenario for its spectral properties.

A characteristic feature of the magnetic properties observed in the '1111' (compounds like LaFeAsO) and '122' pnictide classes is the unusual linear-temperature increase of the paramagnetic susceptibility. There are two explanations of this phenomenon based either on the assumption of strong antiferromagnetic fluctuations in a two-dimensional Fermi liquid, or of peculiarities of the single-particle spectra. The temperature increase of the susceptibility was considered a universal property of the pnictide superconductors and parent systems. By contrast, Cheng et al. reported that in KFe$_2$As$_2$ the magnetic susceptibility increases only at quite low temperatures, i.e., below 100 K, and then decreases slowly at least up to 300 K. The origin of that temperature dependence of the magnetic susceptibility of KFe$_2$As$_2$ and its connection with the magnetic properties of the other end member of the '122' family, BaFe$_2$As$_2$, had not been explained yet. In particular, it was not studied by first-principle methods.

Today the most powerful technique that can account for correlation effects in real compounds and can describe the physics of the correlated paramagnetic phase, is the LDA+DMFT approach. This method combines the advantage of density-functional theory (typically in...
the local density approximation (LDA)) to describe the material-specific electronic structure of a weakly correlated system, with the ability of the dynamical mean-field theory\textsuperscript{24} to treat the complete range of Coulomb correlations between the electrons in partially filled shells.

In this work, we investigate the temperature evolution of the paramagnetic susceptibility in KFe\textsubscript{2}As\textsubscript{2} in the framework of LDA+DMFT. We compare our results with experiments and our previously published LDA+DMFT data\textsuperscript{11} obtained for the isostructural compound BaFe\textsubscript{2}As\textsubscript{2}. Thereby we demonstrate that the mechanism explaining the anomalous temperature behavior of the magnetic susceptibility in iron pnictides proposed in our previous investigations\textsuperscript{10,11} also allows one to understand the difference between the magnetic properties of these compounds and those of KFe\textsubscript{2}As\textsubscript{2}.

II. TECHNICAL DETAILS

In the LDA+DMFT formalism employed here the material-specific band dispersion obtained within LDA is used as a starting point. Then matrix elements of the effective Hamiltonian $H^{\text{LDA}}(k)$ are computed in the subspace of Wannier functions with the symmetry of $p$ and $d$ states using the projection procedure\textsuperscript{25}. In the second step, the Coulomb interaction matrix $U^\sigma_{\sigma'}$, parametrized by the on-site effective Coulomb parameter $U$ and intraatomic exchange parameter $J$, is calculated for each atom with partially filled shells. Finally, the following many-electron Hamiltonian is iteratively solved by DMFT on the Matsubara contour:

$$
\hat{H}(k) = \sum_{k,im,jm',\sigma} (H^{\text{LDA}}_{im,jm'}(k) - H^{\text{DC}}_{im,jm'}) \hat{a}_{k,im\sigma}^\dagger \hat{a}_{k,jm'\sigma} + \frac{1}{2} \sum_{i,m\neq m',\sigma,\sigma'} U_{im,m'\sigma,\sigma'}^\sigma \hat{n}_{im\sigma}^d \hat{n}_{im'\sigma'}^d.
$$

Here $\hat{a}_{k,im\sigma}^\dagger$ is the Fourier transform of $\hat{a}_{im\sigma}$ which creates an electron on the atom $i$ in the state $|m\sigma\rangle$, where $m$ labels the orbitals and $\sigma = \uparrow, \downarrow$ corresponds to the spin projection. The particle number operator $\hat{n}_{im\sigma}^d$ acts on the states localized at the atoms with partially filled shells (Fe-$d$ states in the present study). The term $H^{\text{DC}}$ stands for a double-counting correction which corresponds to the Coulomb interaction energy already accounted for by LDA (see below).

In the present work the LDA band structure is calculated with the ELK full-potential code\textsuperscript{26} with default parameters of the LAPW basis. We use the values of the interaction parameters $U = 3.5$ eV and $U = 0.85$ eV obtained according to the procedure described in Ref.\textsuperscript{26} The DMFT auxiliary impurity problem was solved by the hybridization function expansion quantum Monte-Carlo method\textsuperscript{27}. The double-counting term is a diagonal matrix with only nonzero elements in the $d-d$ block expressed in the form $E^{\text{DC}} = \overline{U}(n_d - 0.5)$, where $n_d$ is the number of Fe-$d$ electrons calculated within LDA+DMFT and $\overline{U}$ is the average Coulomb parameter for the $d$ states. This form of $H^{\text{DC}}$ yields reliable results for magnetic and spectral properties of iron pnictides\textsuperscript{24,26}.

The orbitally-resolved spectral functions $A_i(\omega)$ were computed as the diagonal elements of the real-energy Green function

$$
A_i(\omega) = \sum_{\mathbf{k}} \left[ I(\omega + \mu) - (H^{\text{LDA}}(\mathbf{k}) - H^{\text{DC}}) - \Sigma(\omega) \right]_{ii}^{-1},
$$

where $\mu$ is the chemical potential calculated within DMFT, $\Sigma(\omega)$ is the self-energy obtained with the use of Padé approximants\textsuperscript{28}, and $I$ is the identity matrix.

The uniform magnetic susceptibility $\chi(T)$ was calculated as the response to a small external magnetic field,

$$
\chi(T) = \frac{\Delta M(T)}{\Delta E},
$$

where $\Delta E$ is the energy correction corresponding to the field and $\Delta M = |N_\uparrow(T) - N_\downarrow(T)|$ is the occupation difference between the spin projections.

III. RESULTS

A. Temperature dependence of the uniform magnetic susceptibility

In the upper panel of Fig.\textsuperscript{1} the temperature behavior of the static magnetic susceptibility of KFe\textsubscript{2}As\textsubscript{2} as computed with LDA+DMFT is shown in comparison with the experimental result of Cheng et al\textsuperscript{24}. Both experimental and theoretical curves show a monotonic decrease in the temperature interval from 125 to 300 K. The slope of the calculated curve is in good agreement with experiment, while its absolute value is by about 20% smaller. The maximum in the experimental susceptibility observed at 100 K is not reproduced in the calculation. Temperatures lower than 77 K are not accessible in the present study. The temperature dependence of the LDA+DMFT calculated paramagnetic susceptibility in the other end member of the ’122’ family is shown in the inset of Fig.\textsuperscript{1}. The similarities and differences of the curves are discussed in the Section\textsuperscript{17} The orbitally resolved Fe-$d$ contributions to the total susceptibility are presented in the lower panel of Fig.\textsuperscript{1} The susceptibilities corresponding to the Fe-$d$ orbitals show a decreasing behavior with temperature. The largest contributions come from the $x^2 - y^2$ and $yz$ ($zx$) orbitals.

B. Spectral properties

The orbitally resolved densities of states of KFe\textsubscript{2}As\textsubscript{2} obtained within LDA are shown in the upper panel of Fig.\textsuperscript{2} in comparison with the result obtained for BaFe\textsubscript{2}As\textsubscript{2}. In each case the Fe-$d$ states form a band with total width of $W \approx 4$ eV located in the approximate...
interval (-2, +2) eV. Therefore the on-site Coulomb parameter $U$ is comparable with the band width ($W/U \sim 1$), implying that correlation effects are important. Both compounds have similar shape and relative positions of the spectral functions on the energy axis. However, in the case of KFe$_2$As$_2$ the Fermi level is located approximately 150 meV lower than in BaFe$_2$As$_2$ due to hole doping.

The Fe-$d$ spectral functions of KFe$_2$As$_2$ computed within LDA+DMFT for the temperature window from 77 to 580 K are presented in Fig. 3 along with the result for BaFe$_2$As$_2$. As in other pnictide superconductors the dynamical Coulomb correlations renormalize the spectrum in the vicinity of the Fermi energy and smear some fine details observed within the LDA, but the overall shape of the curves remains unchanged. This renormalization reduces the distance between the peaks in the Fe-$d$ spectral functions and the Fermi energy. In particular, the peak in the $yz(xz)$ spectral function is now significantly closer to the Fermi level compared to that in BaFe$_2$As$_2$.

Quantitatively, the strength of the electronic correlations can be estimated by the increase of the effective masses in comparison with the LDA results. In the case of a single orbital the mass renormalization is expressed by the derivative of the self-energy $\Sigma(\omega)$ as $m^*/m_b = (1 - \partial \text{Re} \Sigma(\omega)/\partial \omega)$, where $m^*$ denotes the effective mass in LDA+DMFT and $m_b$ is the band mass obtained in LDA. In our calculation the self-energy is a diagonal matrix which leads to an orbital dependence of the masses. The calculated values of $m^*/m_b$ for every Fe-$d$ orbital are shown in Table I. The largest mass renormalization, 4.47, corresponds to the $x^2 - y^2$ orbital. Electronic correlations in the other $d$-orbitals are weaker with $m^*/m_b$ ranging from 2.22 to 4.02. The computed values of $m^*/m_b$ are in good agreement with previous theoretical estimations as well as with the ARPES data of Yoshida et al. The result that the electrons in the $|x^2 - y^2|$-derived bands are the most correlated ones followed by the $|yz|$, $|3z^2 - r^2|$, and $|xy|$ states, is in qualitative agreement with the conclusion on the proximity of KFe$_2$As$_2$ to an orbital-selective Mott transition reported by Hardy et al.
The temperature dependence of the uniform magnetic susceptibility of KFe$_2$As$_2$ was investigated within the LDA+DMFT method. The temperature decrease of the computed susceptibility between 125 K to 300 K agrees well with experiment. We found that, similar to other pnictides including the isostructural parent compound BaFe$_2$As$_2$, the Fe-$d$ spectral functions of KFe$_2$As$_2$ show sharp peaks below the Fermi energy. However, these peaks lie significantly closer to the Fermi level than in BaFe$_2$As$_2$. Making use of the scenario developed in our previous study of the magnetic properties of iron pnictides, we conclude that the qualitative difference between the magnetic susceptibilities of the two isostructural end members of the '122' family is due to the smaller separation between the Fe-$d$ spectral functions and the Fermi energy in KFe$_2$As$_2$, which itself is a consequence of the effective hole doping and the stronger correlations in that compound.

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