Electronic Structure of the Heavy Fermion Metal $\mathrm{LiV_2O_4}$

V. I. Anisimov and M. A. Korotin
Institute of Metal Physics, Ekaterinburg GSP-170, Russia

M. Zölfl and T. Pruschke
Regensburg University, Regensburg, Germany

K. Le Hur and T. M. Rice
Theoretische Physik, ETH-Hönggerberg, CH-8093 Zurich, Switzerland

(Received 26 March 1999)

The electronic structure of the first reported heavy fermion compound without f electrons, $\mathrm{LiV_2O_4}$, was studied by an *ab initio* calculation method. As a result of the trigonal splitting and d-d Coulomb interaction, one electron of the $d^{1.5}$ configuration of the V ion is localized and the rest partially fills a relatively broad conduction band. The effective Anderson impurity model was solved by the non-crossing-approximation method, leading to an estimation for the single-site Kondo energy scale T_K. Then, we show how the so-called exhaustion phenomenon of Nozières for the Kondo lattice leads to a remarkable decrease of the heavy-fermion (or *coherence*) energy scale $T_{\mathrm{coh}} \equiv T_K^2/D$ (D is the typical bandwidth), comparable to the experimental result.

PACS numbers: 71.27.+a, 71.15.Mb

Heavy fermion systems are characterized by a large effective quasiparticle mass inferred from the strongly enhanced electronic specific heat coefficient and spin susceptibility at low temperatures [1]. Until recently this effect was observed only for f-electron compounds containing lanthanide or actinide atoms. The transition metal oxide compound $\mathrm{LiV_2O_4}$ is the first reported heavy fermion system without f electrons [2].

$\mathrm{LiV_2O_4}$ has a face-centered-cubic normal-spinel structure. The formal valence of the V ions is $V^{3.5+}$ leading to 1.5 electrons/V in the $3d$ band. The electronic specific heat coefficient $\gamma(T) = C_e(T)/T$ is extraordinarily large for a transition metal compound [$\gamma(1K) \approx 0.42\ \mathrm{J/mol\,K^2}$], decreasing rapidly with the temperature to $\approx 0.1\ \mathrm{J/mol\,K^2}$ at 30 K. The spin susceptibility from 50 to 400 K shows a Curie-Weiss [$\chi = C/(T - \theta)$] behavior corresponding to *weakly* antiferromagnetically coupled ($\theta = -30$ to -60 K) vanadium local magnetic moments with $S = 1/2$ and $g \approx 2$, but static magnetic ordering does not occur above 0.02 K and superconductivity is not observed above 0.01 K. The nearly temperature independent spin susceptibility $\chi(T)$ and Knight shift $K(T)$ for $T < 30$ K are a sign of the disappearance of the V local moment in this temperature region [2].

In the traditional heavy-fermion compounds there are two distinct types of electronic states, the localized f orbitals of lanthanide or actinide atoms which form local moments and the delocalized s, p, and d orbitals which are responsible for the metallic properties. The weak hybridization of the f orbitals with the conduction states leads to the low temperature anomalies. If one of the 1.5 $3d$ electrons per V ion would be in a localized orbital, and the rest in a relatively broad band, then the situation would be analogous to f compounds and all experimental facts could be qualitatively understood [3,4]. As the general opinion was that these 1.5 electrons are in the (same) band formed by t_{2g} orbitals, such a model was considered to be unrealistic. In this paper we will show that the trigonal point group symmetry of the V ion in $\mathrm{LiV_2O_4}$ lifts the degeneracy of the t_{2g} band (see *note added*). As a result, the above-mentioned model is appropriate to estimate the heavy-fermion energy scale for this compound.

The normal-spinel crystal structure is formed by the edge-shared oxygen octahedra with V atoms at the centers and Li atoms between octahedra. The face-centered-cubic lattice has four V atoms in the unit cell which form a tetrahedron (Fig. 1). The total space group of the crystal is cubic but the local point group symmetry of the V-ion crystallographic position is trigonal. The different trigonal axes of every V atom in the unit cell are directed towards the center of the tetrahedron.

The octahedral coordination of the oxygen ions around the V results in the strong splitting of d states into triply degenerate t_{2g} orbitals with lower energy and double degenerate e_g orbitals with higher energy. The band structure has three well-separated sets of bands, completely filled O-$2p$-band, partially filled t_{2g} band, and empty e_g bands. As only partially filled bands are important for the physical properties we will restrict our analysis to the t_{2g} band.

In the trigonal symmetry crystal field the three t_{2g} orbitals are split into the nondegenerate A_{1g} and double degenerate E_g representations of the D_{3d} group. The A_{1g} orbital is $(xy + xz + yz)/\sqrt{3}$ if the coordinate axes are directed along V-O bonds. If the z direction is chosen along the trigonal axis then the A_{1g} orbital is $3z^2 - r^2$

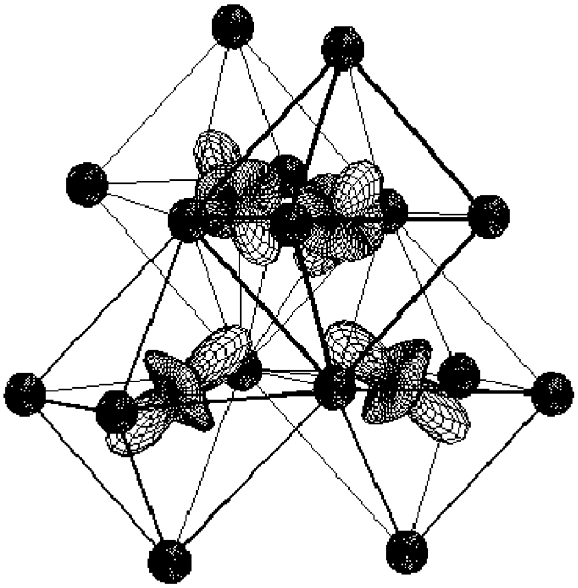

FIG. 1. The four V atoms in the spinel unit cell with the corresponding oxygen octahedra. The angular distribution of the density of $3d$ electrons obtained in the LDA + U calculation (mainly the localized A_{1g} orbitals) is shown.

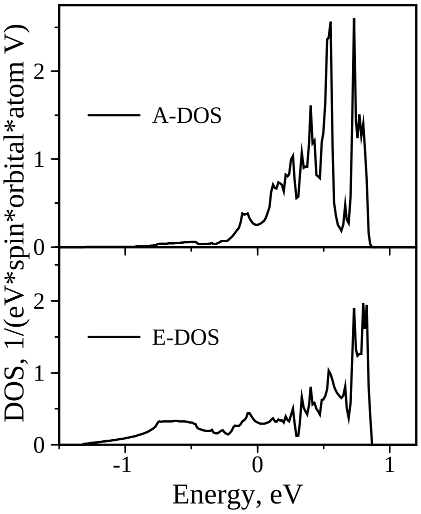

FIG. 2. The density of states (DOS) of t_{2g} band for LiV_2O_4 decomposed in A_{1g} and E_g orbitals obtained in the LDA calculations.

(see Fig. 1) and the E_g orbitals have the lobes in the plane perpendicular to z.

We have performed local-density approximation (LDA) calculations of the electronic structure of LiV_2O_4 by the linear muffin-tin orbital (LMTO) method [5]. In Fig. 2 the results for the t_{2g} band are presented with the partial density of states (DOS) projected to A_{1g} and E_g orbitals. While the partial E_g DOS has the width of ≈ 2 eV, the A_{1g} DOS is much narrower (a width of only ≈ 1 eV). The trigonal splitting is smaller than the bandwidth but it is not negligible. We have estimated it as a difference of the centers of gravities of A_{1g} and E_g DOS's and have found that the energy of the A_{1g} orbital is 0.1 eV lower than the energy of E_g orbitals.

We have calculated the d-d Coulomb interaction parameter U [6] and have found the value of 3 eV, which is larger than the bandwidth $W \approx 2$ eV. Such a value of the U/W ratio leads to the appearance of lower and upper Hubbard bands with one electron localized in the former and the other 0.5 partially filling the latter. Which particular orbital will form the lower Hubbard band is defined by the sign of the trigonal splitting between the energies of A_{1g} and E_g orbitals.

The effect of the d-d Coulomb interaction on the electronic structure of transition metal compounds can be treated by the LDA + U method [7]. This method is basically a combination of the Hartree-Fock approximation to the multiband Hubbard model with LDA. The ground state of the LDA + U solution was found to be indeed a metal with one electron nearly completely localized on the A_{1g} orbital and the E_g orbitals, forming a relatively broad (≈ 2 eV) band which is partially filled.

The partial DOS for E_g orbitals has a long low-energy tail (Fig. 2) and, as a consequence, the LDA occupancy of the E_g orbital is significantly larger than the corresponding value for the A_{1g} orbital. One would expect that, after switching on the Coulomb interaction in the LDA + U calculation, the orbital whose occupation was larger becomes, in the process of the self-consistency iteration, more and more occupied at the expense of all other orbitals and, in the end, the d electron will be localized on one of the E_g orbitals. In reality the situation is more complicated. Indeed, the Coulomb interaction energy will be lowered by the localization of the electron on any orbital. However, the total energy of the solution with the localized electron on the A_{1g} orbital is lower than the energy of the solution with the E_g orbital due to the trigonal splitting. The rotation invariant formulation of the LDA + U method allows the system itself to choose on what particular orbital (or the particular combination of the basis set orbitals) the electrons will be localized. If one starts from the LDA orbital occupancies, rather than at the first stage of the self-consistency iterations the E_g orbital, having a larger LDA occupation becomes localized. However, further iterations cause "rotations" in the five-dimensional space of $3d$ orbitals, leading to the solution with the A_{1g} orbital occupied. The system arrives at this solution independently of the starting point. The total energy as a functional of the orbital occupation matrix has only one minimum, and the corresponding LDA + U equations have only one solution.

The separation of the t_{2g} states into the localized A_{1g} orbital and the conduction band E_g orbitals shows that LiV_2O_4 can be regarded as an analog of f systems. In order to estimate the strength of the interaction between the localized and the conduction electrons we have defined an effective Anderson impurity model. The partial DOS for the A_{1g} orbital obtained in the LDA + U calculation $n_{A_{1g}}(E)$ was used to determine the position of the impurity state ϵ_f and the hybridization function

$\Delta(E)$:

$$n_{A_{1g}}(E) = -\frac{1}{\pi}\,\mathrm{Im}[E - \epsilon_f + i\Delta(E)]^{-1}. \qquad (1)$$

The results are presented in Fig. 3. We then used the LDA + U results as input to estimate the Kondo energy scale for a single-site model. To solve this Anderson *impurity* model we have used a resolvent perturbation theory.

Within this approach, one determines the renormalization of the impurity states by the hybridization with the surrounding medium. The latter is given by the hybridization function $\Delta(E)$. The approach leads to a perturbation expansion in terms of $\Delta(E)$. A widely used approximation, the non-crossing-approximation [8], is well known to reproduce the low-energy scale of the underlying model [9], which is the single-site Kondo temperature T_K. Here we have extracted this quantity directly from the singlet-triplet splitting of the impurity states. For the hybridization function $\Delta(E)$ shown in Fig. 3 we estimate for the single-site Kondo temperature $T_K \approx 550$ K. On the other hand, the Kondo temperature can be expressed via a Kondo parameter J_K as [10]

$$T_K = De^{-1/2N(0)J_K}, \qquad (2)$$

where D is the effective Fermi energy and $N(0)$ is the density of conduction states per spin. In Ref. [3] the value of $N(0)$ was estimated from the experimental value of the Pauli susceptibility as 2.9 states/(eV vanadium spin direction). With a D value of approximately 1 eV, this gives us an estimation for $J_K \approx 670$ K.

In contrast to standard f systems where the direct exchange between localized f electrons and conduction electrons is small, both localized and conduction electrons are $3d$ electrons in our case and there is a strong on-site exchange coupling between them, namely, a ferromagnetic Hund coupling of the order of 1 eV. The presence of two types of d electrons, namely, those in conduction states and the electrons forming local moments, is known to result in a lattice in a double exchange ferromagnetic interaction between local moments. We have estimated this value of the intersite exchange coupling parameter from the results of the LDA + U calculation using the formula derived as a second derivative of the total energy with respect to the angle between local moment directions [11]. Our calculation gave the value of the double exchange parameter $J_{\mathrm{dex}} = 530$ K.

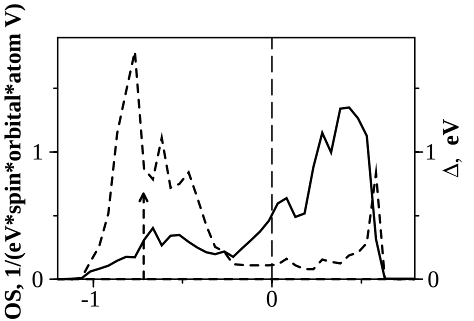

FIG. 3. The parameters of the effective Anderson impurity model. Solid line—hybridization function $\Delta(E)$; dashed arrow—the position of the impurity state ϵ_f; dashed line—the partial DOS for the A_{1g} orbital obtained in the LDA + U calculation $n_{A_{1g}}(E)$.

However, there is another contribution to the interaction between the local moments. The Kondo exchange is between a local moment (electron on the A_{1g} orbital) on one site and the spin of the conduction electron (E_g orbital) on the neighboring site because, having different symmetry the orbitals do not mix on the same site. As the spins of the E_g and A_{1g} electrons on the neighboring site are "strongly" coupled by the Hund interaction, it gives us an effective antiferromagnetic (AF) interaction between local moments on neighboring sites approximately equal to the Kondo exchange parameter J_K. As a result there is a strong cancellation between these two processes, ferromagnetic double exchange and AF Kondo-induced exchange, so that the net exchange interaction is small. Simply subtracting the two terms leads to an estimate J_K-$J_{\mathrm{dex}} \sim 140$ K. The measured Curie-Weiss Θ at high temperature ($\Theta \sim 50$ K) points to a more complete cancellation and a net AF exchange interaction that is an order of magnitude smaller than our estimate. This discrepancy is not surprising in view of the difficulty of making a reliable estimate in the presence of this strong cancellation. Note that the inherent frustration that inhibits the onset of AF order in a spinel lattice does not enter the determination of the value of Θ. The small value of Θ shows that the net exchange interaction between neighboring local moments is very weak.

A realistic lattice model for LiV_2O_4 contains two competing terms which couple the conduction and localized states. These are the on-site Hund's ferromagnetic coupling and the AF Kondo interaction which couples conduction and localized electrons on neighboring sites. This competition makes difficulties for a first principles treatment. On the other hand, there are several arguments in favor of ignoring the ferromagnetic interactions relative to the Kondo interaction. For a single localized site, it is well known that the on-site ferromagnetic coupling between conduction and localized states scales to the weak coupling limit at low temperatures and so can be ignored. However, it could be argued that in the lattice this ferromagnetic coupling scales to the strong coupling limit through the well-known double exchange effect. But as discussed above, the double exchange effect is canceled here by the AF interaction between the localized spins induced by the Kondo effect. Therefore it seems plausible to ignore, at least as a first step, the ferromagnetic interactions and treat only the AF interaction so that the model is simply a Kondo lattice model. There may be some renormalization of the Kondo exchange parameter, J_K but for now we ignore that also.

In the Kondo lattice model there is also competition between the induced AF interactions, which favor AF order, and the Kondo effect, which favors a singlet ground state [12]. Here, the former are very weak due to the cancellation effects discussed above and, as a result, we are in the limit where the Kondo effect dominates. This leads to the formation of a heavy-fermion Landau Fermi liquid with a characteristic temperature scale for the onset of quantum coherence, T_{coh}. The exact value of T_{coh} is difficult to estimate but there are a number of strong arguments that $T_{\mathrm{coh}} \ll T_K$, the single-site Kondo temperature. We summarize these arguments below.

In the single-site case, the local moment forms a singlet pair with *any* conduction electron within an energy T_K of the Fermi energy. We have the picture of a complex screening cloud which delocalizes the impurity at the Fermi level. The resulting nonperturbative ground state is found to be of a Fermi-liquid-type [13,14], where all of the physical quantities depend on T_K. In the concentrated Kondo lattice, the number of conduction electrons per site to screen the local moments is of order $n_k = \frac{T_K}{D} \ll 1$. There is a lack of conduction electrons to screen all the spin array at the energy scale T_K: this is the well-known *exhaustion* phenomenon [15]. In that sense, a macroscopic singlet ground state should not take place at T_K, but rather at a very low temperature T_{coh}. To obtain it, we can use the following simple thermodynamical arguments. The condensation energy that we really dispose to screen the (effective) localized spins is: $\mathrm{E}_{\mathrm{cond}} = N_V n_k T_K$, where N_V is the total number of V ions (we have 1 localized $3d$ electron per V). In order to stabilize a perfect singlet ground state, this energy must absorb all the entropy of the impurity lattice which is defined as $S_{\mathrm{tot}} = N_V \ln 2$. Then, the energy scale at which the entropy of the spin array will go to zero can be simply defined as $T_{\mathrm{coh}} = E_{\mathrm{cond}}/S_{\mathrm{tot}} \simeq n_k T_K = T_K{}^2/D$ [16]. For $T \ll T_{\mathrm{coh}}$, the prevalent bonds should be formed between local moments and then T_{coh} plays the role of the effective Kondo temperature in the lattice problem [17]. It should be noted that these effects predicted by physical arguments were recently observed in calculations for the periodic Anderson model in the framework of the dynamical mean-field theory [18]. Taking into account the estimations for T_K and D, we obtain $T_{\mathrm{coh}} \sim 25-40$ K, which agrees well with the numerical result for the periodic Anderson model [19]. It also seems to be in good agreement with the experimental result in $\mathrm{LiV_2O_4}$. This should produce an enhanced linear specific heat and Pauli susceptibility, which are proportional to N_V/T_{coh}, and a (normalized) Wilson ratio R_W, which is equal to 1 [17]. Experimentally, R_W is on the order of unity as in conventional heavy metals [2].

In conclusion, our calculations using the LDA + U method give a theoretical justification of a model with one of the $3d$ electrons per V localized in a A_{1g} orbital and the remaining 0.5 electron/V in a conduction band state, primarily of E_g symmetry, which has been previously discussed [3,4]. This leads to a lattice model with competing on-site ferromagnetic coupling due to the Hund's rule and nearest neighbor antiferromagnetic coupling due to the Kondo effect. We present arguments that such a model reduces to a Kondo lattice model. Estimates for the temperature scale for the onset of quantum coherence give a small value, much less than the single site Kondo temperature, in agreement with experiments. The low temperature heavy-fermion Fermi liquid is strongly correlated and is therefore a good candidate for a transition to unconventional superconductivity, if it can be made perfect enough.

We thank D. Johnston, D. Khomskii, and D. Cox for stimulating discussions. This work was supported by the Russian Foundation for Basic Research (Grants No. RFFI-98-02-17275 and No. RFFI-96-15-96598).

Note added.—Recently, an LDA calculation of the electronic structure of $\mathrm{LiV_2O_4}$ was made by Eyert *et al.* [20], where the partial density of states of the t_{2g} band was analyzed using trigonal symmetry, but the possibility of orbital polarization of electrons due to the Coulomb interaction was not investigated.

[1] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, England, 1993).

[2] S. Kondo *et al.,* Phys. Rev. Lett. **78**, 3729 (1997).

[3] A. V. Mahajan, R. Sala, E. Lee, F. Borsa, S. Kondo, and D. C. Johnston, Phys. Rev. B **57**, 8890 (1998).

[4] For recent reviews, see D. C. Johnston, C. A. Swenson, and S. Kondo, cond-mat/9811411; S. Kondo, D. C. Johnston, and L. L. Miller, cond-mat/9812020.

[5] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); we have used Stuttgart TBLMTO-47 computer code.

[6] O. Gunnarsson, O. K. Andersen, O. Jepsen, and J. Zaanen, Phys. Rev. B **39**, 1708 (1989); V. I. Anisimov and O. Gunnarson, Phys. Rev. B **43**, 7570 (1991).

[7] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991); V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys. Condens. Matter **9**, 767 (1997).

[8] H. Keiter and J. C. Kimbal, J. Magn. **1**, 233 (1971).

[9] E. Müller-Hartmann, Z. Phys. B **57**, 281 (1984).

[10] K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975).

[11] A. I. Lichtenstein *et al.,* J. Magn. Magn. Mater. **67**, 65 (1987); A. I. Lichtenstein, J. Zaanen, and V. I. Anisimov, Phys. Rev. B **52**, R5467 (1995).

[12] S. Doniach, in *Valence Instabilities and Narrow Band Phenomena,* edited by R. Parks (Plenum, New York, 1977), p. 34; Physica (Amsterdam) **91B**, 231 (1977).

[13] Ph. Nozières, J. Low Temp. Phys. **17**, 31 (1974).

[14] N. Andrei, Phys. Rev. Lett. **45**, 379 (1980); P. B. Wiegmann, JETP Lett. **31**, 364 (1980).

[15] Ph. Nozières, Ann. Phys. (Paris) **10**, 19 (1985).

[16] Ph. Nozières, Eur. Phys. J. B **6**, 447 (1998).

[17] K. Le Hur, Phys. Rev. B **58**, 10 261 (1998).

[18] A. N. Tahvildar-Zadeh, M. Jarrell, and J. K. Freericks, Phys. Rev. Lett. **80**, 5168 (1998); Th. Pruschke and R. Bulla (to be published).

[19] T. Pruschke (to be published).

[20] V. Eyert *et al.* (to be published).