Comment on Phys. Rev. Lett. paper: "LiV$_2$O$_4$: A heavy fermion transition metal oxide"

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An interpretation of electronic and magnetic properties of LiV$_2$O$_4$, including the heavy-fermion behavior, reported by Kondo *et al.* (Phys. Rev. Lett. **78** (1997) 3729) with localized *d*-electrons, has been presented as being superior to a Fermi-liquid delocalized *d*-electron model. It is pointed out that crystal-field and relativistic effects are very important for details of the low-energy, <10 meV, electronic structure.

Kondo *et al.* [1] have announced LiV$_2$O$_4$ as a first *d*-electron material exhibiting heavy-fermion (h-f) behavior characteristic of those of the heaviest-mass *f*-electron systems. For the understanding of these phenomena authors recall the Fermi-liquid interpretation. In description of LiV$_2$O$_4$ the authors have written that it contains equivalent V ions in sligthly distorted octahedral coordination. The Curie constant is consistent with a V^{4+} spin S=1/2, i.e. with one d electron.

By this Comment I would like to put attention that there exists a theoretical model, another than the Fermi-liquid model based on the delocalization of *f/d* electrons, that can account for the heavy-fermion behavior for compounds with 3*d* paramagnetic ions [2–4]. This model bases on the localized picture for the *f/d* electrons and underlines the importance of the crystal field (CEF) interactions. This model, though originally developed for *f*-electronic systems, **has predicted** the h-f behavior for 3*d* paramagnetic systems (Ref. [3], pages 2 and 35).

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According to this model "the heavy-fermion behavior is expected for (intermetallic and ionic) compounds containing Kramers ions, i.e. the highly-correlated electronic systems f^n/d^n with an odd number n of electrons." Such the systems have the doubly-degenerated ground state (Kramers doublet) as the charge-formed ground state. Its degeneracy has to be removed before the system reaches the absolute-zero temperature. When spin interactions are weak or the involved local moments are small the splitting is small and the large heat appears at low temperatures.

I believe that in LiV_2O_4 the observed metallic behavior is due to the $2s^1$ electron of Li and there exists V^{4+} ions with one d electron. In the octahedral cubic crystal field, the T_{2g} state is the ground state of the localized d^1 system [5]. It is the 6-fold degenerated state in the orbital+spin space. The spin-orbit (s-o) coupling splits [6] it into lower quartet and the higher doublet separated by $3/2\lambda$ ($\lambda = +360$ K; Ref. 5 p. 399; 1 meV $= 11.6$K $= 8$cm^{-1}). Any tetragonal or trigonal distortion splits the lower quartet into two doublets with the separation dependent on the magnitude of the lattice distortion. Extremely interesting is that the magnetic moment of the lower quartet is zero. This magnetic moment as well as the fine electronic structure can be calculated by the consideration of a single-ion Hamiltonian of the form [6]:

$$H_d = B_4 \ (O_4^0 + 5O_4^4) + \lambda \ \mathbf{L} \cdot \mathbf{S} + B_2^0 O_2^0 + \mu_B (\mathbf{L} + g_s \mathbf{S}) \cdot \ \mathbf{B}_{ext} \ (1).$$

The first term is the cubic CEF Hamiltonian with the Stevens operators O_n^m that depend on the orbital quantum numbers L, L_z. The second term accounts for the spin-orbit coupling with λ as the s-o constant. The third term is a tetragonal lattice distortion. The last term allows for calculation of the influence of the external magnetic field. The Hamiltonian (1) is considered in the $|LSL_zS_z >$ base [7] with L and S fulfilling the two first Hund's rules: S=1/2 and L=2. By the direct diagonalization of the 10x10 matrix, associated with the parameters $B_4 = +200$ K, $B_2^0 = +6$ K and $\lambda = 360$ K one obtains three low-lying doublets at 0, 35 K and 570 K (originated from the cubic T_{2g} state) and a quasi-quartet at 24180 and 24250 K (the cubic E_g state). An extremally small magnetic moment of the ground state of ± 0.001 μ_B results from the almost perfect cancellation of the spin and orbital moment caused by the spin-orbit coupling. The excited state at 35 K is magnetic. It produces an anomalous temperature dependence of the susceptibility with a maximum [8] like is observed. The calculated plot χ^{-1} *vs* T points to a large negative Weiss temperature what is a purely CEF effect. The existence of the localized state at 35 K is seen in the Schottky-type specific heat

centered at 16 K. The calculations yield the maximum of 3.6 J/K mol in very good agreement with experimental data.

In conlusion, intriguing electronic and magnetic properties of LiV_2O_4, including the heavy-fermion behavior, can be well understood within the individualized-electron model [2–4] that treats d electrons as largely localized. The heavy-fermion behavior is related with the Kramers-doublet charge-formed ground state of the localized d^1 electronic system of the V^{4+} ion. For the description of the low-energy, <10meV, electronic structure a relativistic effect, the spin-orbit coupling, and CEF interactions have to be taken into account.

I argue that this description is superior to the Fermi-liquid description used by Kondo *et al.*.

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[7] the computer program is available on the written request to the author.
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