Structure and Thermal Expansion of LiV_2O_4: Correlation between Structure and Heavy Fermion Behavior

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The structural properties of the heavy fermion (HF) transition metal oxide LiV_2O_4 have been studied as a function of temperature T from 4 to 295 K. Upon cooling from 295 K the lattice parameter a contracts gradually to become nearly constant between 65 and 20 K and then decreases again below 20 K. The downturn in $a(T)$ below 20 K correlates with the crossover from local moment to HF behavior. The thermal expansion is found to depend predominantly on the interatomic Li-O bonds while V-O bond lengths change only slightly. The electronic Grüneisen parameter at 7 K is inferred to be large (~ 25), similar to low-T values of some f-electron HF compounds. [S0031-9007(97)04794-7]

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The recent discovery by Kondo *et al.* [1] of heavy fermion (HF) behavior in LiV_2O_4, with a Kondo or spin fluctuation temperature $T_K \sim 28$ K, is of particular importance because it is the first d-electron material to exhibit HF behaviors characteristic of those observed for the heaviest-mass f-electron systems. This compound shows neither static magnetic ordering nor superconductivity above 0.02 K [1]. LiV_2O_4 was reported by Reuter *et al.* [2] in 1960, to crystallize in the fcc normal spinel structure containing equivalent vanadium ions in slightly distorted octahedral coordination by oxygen.

Rogers *et al.* [3] and Faran *et al.* [4] prepared single crystals and O-deficient polycrystalline samples, respectively, showing metallic behavior in the resistivity ρ. Moreover, a pronounced smooth downturn occurs in the $\rho(T)$ of single crystals below 30 K [3], consistent [1] with Kondo lattice behavior in which the onset of electronic coherence below T_K reduces ρ [5]. The recent magnetic susceptibility, heat capacity, and ^{7}Li NMR measurements reported by Kondo *et al.* [1] showed a crossover, with decreasing temperature below $T_K \sim 28$ K, from localized moment to the heavy fermion behavior. In an attempt to investigate a possible structural response to this crossover, a detailed neutron study has been carried out from room temperature to 4 K. In this Letter, we report the discovery of extraordinarily strong coupling of the structure to the electronic degrees of freedom in LiV_2O_4. In particular, we find that the volume thermal expansion coefficient β increases strongly below $\sim$20 K $\sim T_K$ to a value $\sim 6 \times 10^{-6}$ K^{-1} at $\sim$7 K, an order of magnitude or more larger than obtained for conventional metals at this temperature. This large β is correlated with the large electronic heat capacity C_e found at low T for LiV_2O_4 in Ref. [1]. The normalized ratio of β to C_e at low temperatures, where the lattice heat capacity is very small relative to that of the conduction electrons, is called the electronic Grüneisen parameter Γ_e. We find that $\Gamma_e(7\text{ K}) \sim 25$, again roughly an order of magnitude larger than in conventional metals. This value is, however, similar to those of some f-electron HF metals at low T (see below). Thus, the HF-lattice coupling in LiV_2O_4 is much stronger than in conventional metals, even when normalized by the large C_e. Our results provide essential input for a theory of the mechanism for the formation of the HF state in LiV_2O_4, which is currently unknown.

Polycrystalline LiV_2O_4 samples were synthesized using the techniques described in Ref. [6] and were single phase as determined by neutron diffraction. Our sample is "sample 5" of Ref. [1]. Neutron diffraction data were collected on the Special Environment Powder Diffractometer [7] at Argonne's Intense Pulsed Neutron Source over the temperature range 4–295 K with the sample in helium exchange gas. Enough delay time (typically 40 min) was allowed at each temperature to ensure that thermal equilibrium was reached before data were collected. Below 20 K, data were collected repeatedly after both cooling or heating to ensure reproducibility of the results. Structures were refined by the Rietveld method using the (General Structure Analysis System) GSAS code [8].

The structure of LiV_2O_4 is cubic, space group $Fd3m$, at all temperatures. No phase transition, extra lines, or unusual thermal factors were observed down to 4 K. These results are consistent with the x-ray diffraction measurements in Refs. [1,9] which showed no evidence for structural transitions down to 9 and 8 K, respectively. Refined structural parameters at selected temperatures are given in Table I. Because V atoms have such a small and negative scattering length for neutrons ($b = -0.04 \times 10^{-12}$ cm), the negative temperature factors for V are not physically meaningful and the other refined

TABLE I. Refined structural coordinates and R factors for LiV_2O_4 at different temperatures. Cubic structure of space group $Fd3m$ with Li, V, and O at $(1/8, 1/8, 1/8)$, $(1/2, 1/2, 1/2)$, and (x, x, x), respectively.

T (K)	295	250	200	150	100	50	15	4
a (Å)	8.24039(3)	8.23605(4)	8.23177(4)	8.22889(4)	8.22737(3)	8.22688(3)	8.22687(3)	8.22672(3)
B(Li) (Å^2)	1.10(5)	1.08(6)	1.06(6)	0.85(6)	0.81(6)	0.79(6)	0.73(3)	0.72(3)
B(V) (Å^2)	−0.29(6)	−0.32(8)	−0.24(8)	−0.24(8)	−0.45(7)	−0.50(5)	−0.46(5)	−0.50(5)
x(O)	0.26127(2)	0.26128(3)	0.26118(3)	0.26114(3)	0.26110(3)	0.26112(3)	0.26114(2)	0.26111(2)
B(O) (Å^2)	0.48(1)	0.41(2)	0.38(2)	0.33(2)	0.27(1)	0.27(1)	0.26(1)	0.24(1)
R_p	4.07	5.28	5.50	5.79	5.49	5.36	4.31	3.91
R_{wp}	5.98	8.40	8.63	9.04	8.42	8.32	6.43	5.82
R_I	4.88	5.34	7.48	7.13	5.42	5.62	6.89	5.85
χ^2	1.550	1.300	1.268	1.256	1.314	1.298	1.523	1.297

values are the same if this parameter is fixed at any reasonable value. Selected interatomic bond lengths and bond angles calculated using the refined structural parameters are given in Table II. The diffraction data and best-fit Rietveld profile at 4 K and at 295 K are shown in Fig. 1.

The structure of LiV_2O_4 is shown in Fig. 2. The LiV_2 substructure is identical to the AB_2 cubic laves phase ($C15$) structure. Vanadium atoms are sixfold coordinated by O. The coordination polyhedron may be described as a slightly distorted octahedron with six equivalent V-O distances of ~1.9716 Å at room temperature. The structure can be described as a stack of layers containing chains of these edge-sharing V octahedra parallel to each other within the plane. The direction of these chains is rotated by 90° in the layers directly above and below. The successive layers are interconnected through the top of the vanadium octahedra. Lithium atoms are tetrahedrally coordinated by four oxygen atoms and are located in the cavities that form between the chain layers. Lithium-oxygen tetrahedra share their corners with the neighboring vanadium-oxygen octahedra. At room temperature, the Li-O distances and the O-Li-O angles are about 1.9450 Å and 109.47°, respectively.

The cubic lattice parameter a as a function of temperature is plotted in Fig. 3. The figure shows a monotonic decrease upon cooling. The thermal expansion decreases at lower temperatures. From 65 to ~20 K the lattice parameter remains nearly constant before starting to decrease again around 20 K (see inset of Fig. 3). The decrease below 20 K is very small, but is reproduced in repeated measurements upon both heating and cooling.

TABLE II. Interatomic distances and bond angles for LiV_2O_4 at different temperatures.

T (K)	Li-O (Å)	O-Li-O (deg)	V-O (Å)
295	1.9450(3)	109.47	1.9716(2)
250	1.9441(4)	109.47	1.9705(2)
200	1.9416(4)	109.47	1.9702(2)
150	1.9404(4)	109.47	1.9698(2)
100	1.9395(4)	109.47	1.9697(2)
50	1.9396(4)	109.47	1.9695(2)
15	1.9399(3)	109.47	1.9693(2)
4	1.9393(3)	109.47	1.9696(2)

Figure 4 shows the temperature dependence of the Li-O and V-O bond lengths. The normalized lattice parameter a and interatomic bond lengths are shown in Fig. 5 as a function of temperature. The latter figure shows a greater temperature dependence of the Li-O bond lengths compared to that of the V-O bonds. The thermal expansion for the Li-O bonds, [defined as $(1/L_0)(\partial L/\partial T)$], is about 2 and 3.5 times larger than that of the lattice parameter a and the V-O bonds, respectively.

Figure 6 shows the molar electronic specific heat C_e [1] and the lattice parameter a versus temperature below 80 K. These two quantities are correlated below ~20 K, indicating a strong coupling between the electronic and

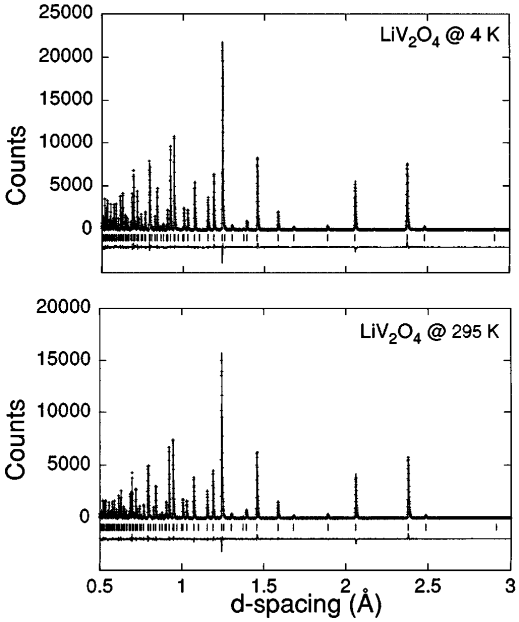

FIG. 1. Neutron diffraction data and best-fit Rietveld profile at 4 and 295 K. (+) are the observed neutron data; solid line is the calculated intensities. Tick marks show the locations of allowed Bragg peaks. The difference curve is shown at the bottom of each figure.

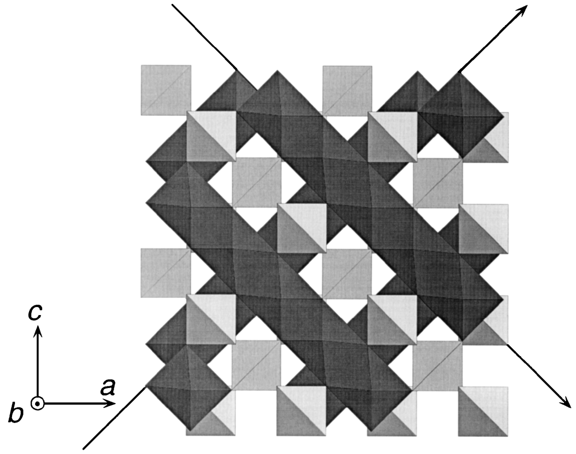

FIG. 2. Structure of LiV_2O_4. For clarity, only two layers are shown.

lattice degrees of freedom as the system crosses over to HF behavior with decreasing T below T_K. The relationship between C_e and the low-T volume thermal expansion coefficient β in f-electron HF compounds is often discussed in terms of an electronic Grüneisen parameter Γ_e, given [10] by

$$\Gamma_e(T) = V_m \beta(T)/\kappa C_e(T), \quad (1)$$

where V_m is the molar volume and κ is the compressibility. Γ_e generally increases with decreasing T and approaches a constant value (for $T \ll T_K$) which is much larger than the value of order unity typical of conventional metals. Here we obtain a rough estimate of Γ_e at low T for LiV_2O_4 as follows. From Fig. 6 we obtain $V_m = 4.19 \times 10^{-5}$ m^3/mol. A linear fit of our $a(T)$ data in Fig. 6 between 4 and 10 K yields the slope α and then $\beta = 3\alpha/a \sim 6 \times 10^{-6}$ K^{-1}. From Fig. 6, $C_e(7\text{ K}) \sim$ 2 J/mol K. For similar oxides like Fe_2O_3, Fe_3O_4, $FeTiO_3$, MgO, TiO_2 (rutile) and the spinel prototype $MgAl_2O_4$, κ is in the range $(0.5 \pm 0.1) \times 10^{-11}$ m^2/N [11]. Combining these values according to Eq. (1) yields $\Gamma_e(7\text{ K}) \sim$ 25. This Γ_e for LiV_2O_4 (which has an electronic specific heat coefficient $\gamma(T) \equiv C_e(T)/T$ of 0.42 J/mol K^2 at $T = 1$ K [1]), is comparable to low-T Γ_e values for f-electron HF compounds such as UPt_3 (71), UBe_{13} (34), and $CeCu_6$ (57) with $\gamma = 0.43$, 0.78, and 1.67 J/mol K^2, respectively [10].

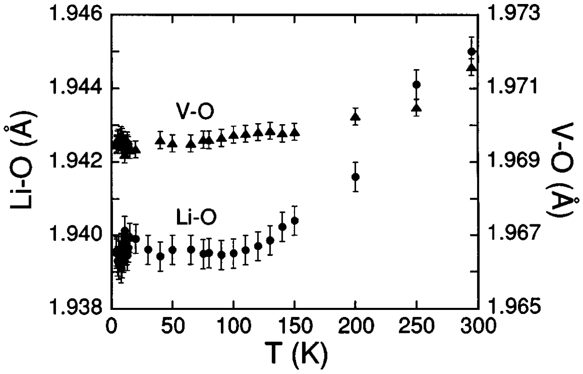

FIG. 4. Temperature T dependence of Li-O and V-O bond lengths.

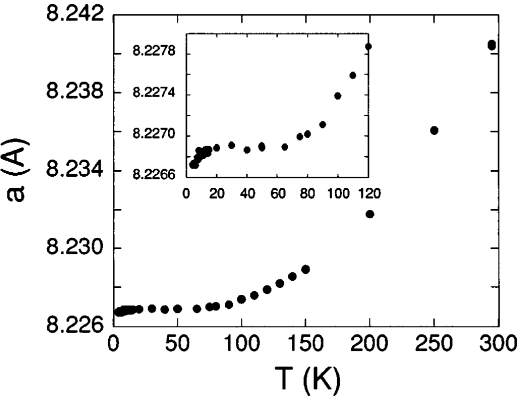

FIG. 3. Lattice parameter a as a function of temperature T.

To conclude, we find that a strong coupling of the electronic degrees of freedom to the lattice exists in the HF regime in LiV_2O_4, similar to the f-electron HF systems. In the f-electron materials, this coupling is thought to originate mainly from a strongly volume strain-dependent hybridization of the f-electron orbitals with those of the conduction electrons [10,12]. However, in LiV_2O_4, the nature of the coupling is at present unclear because the occupied orbitals giving rise to the metallic heavy fermion behavior at low T, and to the combined metallic and (quasi)localized moment behavior at high T, are all apparently the same t_{2g} vanadium d orbitals [13]. Indeed, even the mechanisms by which these low- and high-T behaviors occur in LiV_2O_4 are themselves not yet understood. The variations in the bond lengths and bond angles with temperature in Table II and Figs. 4 and 5 may be relevant to clarifying these mechanisms. In addition, the geometric frustration for antiferromagnetic ordering inherent in the

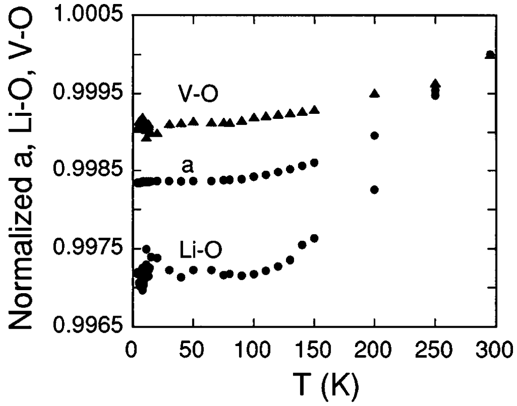

FIG. 5. Normalized lattice parameter a, and Li-O and V-O bond lengths as a function of temperature T.

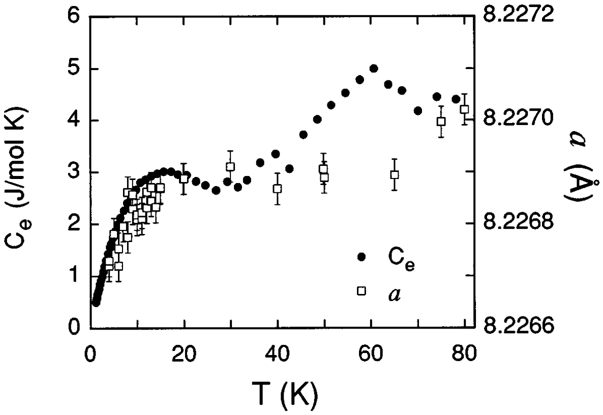

FIG. 6. Electronic specific heat C_e [1] and lattice parameter a versus temperature T below 80 K.

vanadium sublattice of the normal spinel structure may be involved at low T, as suggested in Ref. [1].

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Note added.—After submission of our paper, high resolution thermal expansion measurements of LiV_2O_4 were carried out from 4 to 300 K using capacitance dilatometry [14]. The results are in good agreement with our $a(T)$ data and confirmed our discovery of an extremely strong increase in the thermal expansion coefficient below 20 K.

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