Comparison of the Temperature Dependence of the Crystal Structure of $LiTi_2O_4$ and LiV_2O_4

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The normal spinel oxide $LiTi_2O_4$ is an exotic superconductor with $T_c = 11.2$ K, while the isostructural neighbouring LiV_2O_4 exhibits heavy-fermion behaviour. The origin of their physics and the role of the spinel structure on their properties are yet unsolved issues, owing mainly to the complexity of the structure, the presence of subtle disorder, and the sample dependence of the physical properties. Especially and perhaps more importantly, the enormous difference in their low-temperature properties remains an open question. This question has only been addressed theoretically but (mainly because of the above problems) there were no experimental studies that sought to understand the clearly distinct behaviour of the two systems. Here, we contribute to the understanding of such distinct low-temperature behaviour by comparing the temperature dependence of the very basic structural properties of the two systems. Upon cooling from room temperature, the lattice parameter a decreases gradually in about the same way for both systems. However, below 20 K, a clear decrease in a of LiV_2O_4 as a function of temperature contrasts strongly with the almost constant value of a of $LiTi_2O_4$ in the same temperature range. Therefore subtle but clearly different structural signatures are coupled with the very divergent physical properties of the two systems and suggest new directions to the theory.

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1. Introduction

The exploration of fundamental phenomena like superconductivity and heavy-fermion behaviour in crystal lattices which are not common host of them, offers the unique possibility to address the very basic question on what is essential or not for the appearance of such phenomena. The neighbouring compounds $LiTi_2O_4$ and LiV_2O_4 are notable examples within this context and, because of their uniqueness, intrigued solid state scientists for more than three decades. $LiTi_2O_4$ is the only oxide superconductor adopting the spinel structure [1]. LiV_2O_4 on the other hand, is the only oxide heavy-fermion (HF) material with spinel structure and one of the extremely rare examples of d-electron metals exhibiting heavy Fermi liquid behaviour [2]. Whether the spinel structure itself influences or even favours

the appearance of superconductivity in $LiTi_2O_4$ and of HF behaviour in LiV_2O_4 is currently an outstanding open question. A related and perhaps more concrete question is why there is such a dramatic difference between the low-temperature properties of these two next neighbouring materials and whether lattice effects contribute to or even impose such difference.

$LiTi_2O_4$ belongs to the normal spinel structure. Details on the crystal structure, defects, and disorder as well as on their influence on the superconducting parameters and on the physical properties of the compound are given in Refs. [1, 3] and [4]. Since in the stoichiometric, ordered material all Ti-cations occupy the equivalent crystallographic sites 16d, $LiTi_2O_4$ is a mixed valence compound with equal ratio of Ti^{3+} which has spin $S = 1/2$ and Ti^{4+} which has $S = 0$. The material is a metal simply due to symmetry considerations. Below the critical temperature $T_c \approx 11.2$ K, it exhibits superconductivity, however the mechanism of superconductivity is yet an open issue. $LiTi_2O_4$ has been reported to be a Bardeen, Cooper, Schrieffer (BCS), resonating valence bond (RVB) or bipolaronic and more recently an exotic superconductor.

The isostructural compound LiV_2O_4 which is the next closest neighbour to $LiTi_2O_4$, is also a mixed valence system with equal ratio of V^{3+} which has spin $S = 1$ and V^{4+} which has $S = 1/2$. Similarly to $LiTi_2O_4$, LiV_2O_4 is metallic. On the other hand, LiV_2O_4 exhibits local moment behaviour above about 28 K which strongly contrasts with the relatively temperature independent Pauli paramagnetism of $LiTi_2O_4$. Furthermore, in striking contrast to $LiTi_2O_4$, LiV_2O_4 exhibits HF behaviour at low-T with the Kondo temperature $T_K \approx 28$ K. The highest purity samples have electronic coefficient of specific heat $\gamma \equiv C/T \approx 420$ mJ/(mol K^2) at 1 K which is the highest value ever observed for any metallic non-magnetic d-metal.

The enormous difference in the properties of the two compounds attracted the attention of the scientific community early after the discovery of HF behaviour in LiV_2O_4. Varma [5] addressed the problem theoretically and explained qualitatively this difference by taking into consideration that $LiTi_2O_4$ contains only one magnetic ion while LiV_2O_4 contains two magnetic ions and therefore the magnetic moment renormalisations in LiV_2O_4 proceed in two stages resulting in enhancement of the effective mass.

Here we present another approach to explain the difference of the physical properties of $LiTi_2O_4$ and LiV_2O_4. We investigated subtle structural changes of the lattices of $LiTi_2O_4$ and especially of the cell constant a as the temperature decreases down to 4 K and compare it with the one of LiV_2O_4.

2. Crystal structure versus T for $LiTi_2O_4$ and LiV_2O_4

$LiTi_2O_4$ powders were synthesised by conventional dry powder processing [6] via the reaction $Li_2O + Ti_2O_3 + 2TiO_2 \rightarrow 2LiTi_2O_4$. The T_c of the material determined by dc magnetization measurements is $T_c = 12.5(\pm 0.2)$ K.

Neutron diffraction experiments were carried out at the High-Resolution Powder Diffractometer (HRPD) at the ISIS Facility, UK. Data were collected at temperatures 300, 200, 100, 15, 14, 13, 12, 11, 10 and 2 K. The neutron diffraction data were analysed by the Rietveld method using the general structure analysis system (GSAS) [7]. The indicators of the quality of the refinements or residuals, χ^2 and R_p, had final values $\chi^2 = 2.925$ to 1.616 and $R_p = 9.46\%$ to 6.5% for the various temperatures. In the final refinement cycles, the occupancies of the octahedral and tetrahedral sites were refined together with the other parameters in order to determine the exact composition of the sample and to check for site-disorder effects. It was found that the material is ordered $Li_{0.98(4)}Ti_2O_4$. Figure 1 shows the temperature dependence of the lattice parameter, a, of $Li_{0.98(4)}Ti_2O_4$ as deduced from the refinements of our neutron diffraction data. Upon cooling from room temperature (RT) to 2 K the lattice parameter contracts gradually to become nearly constant below 15 K, i.e. around and below the superconducting transition $T_c = 12.5(\pm 0.2)$ K. The evolution of other crystallographic parameters will be reported in detail elsewhere.
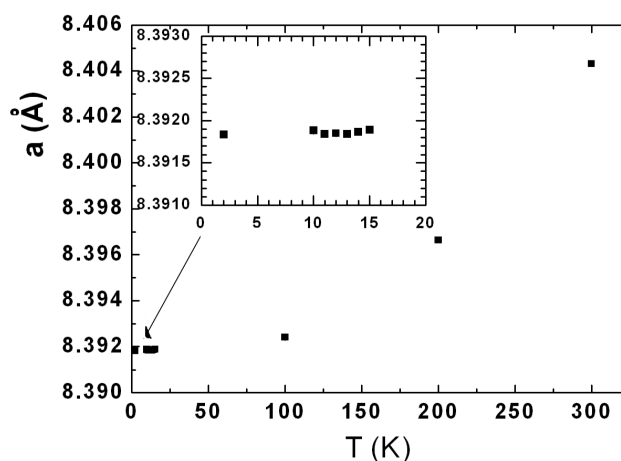

Fig. 1.   Variation of the lattice parameter a of $LiTi_2O_4$ as a function of temperature. Inset: temperature dependence of a of $LiTi_2O_4$ in the temperature range from 0 K to 20 K, i.e. above and below the superconductor transition ($T_c = 12.5(\pm 0.2)$ K).

We now turn to the evolution of the structure of LiV_2O_4 as a function of temperature, reported by Chmaissem et al. [8] and deduced from neutron diffraction data collected on the Special Environment Powder Diffractometer (SEPD) at Argonne's Intense Pulsed Neutron Source. SEPD has lower resolution than HRPD. Upon cooling from RT down to about 65 K, the lattice constant a of LiV_2O_4 decreases monotonically, similarly to the one of $LiTi_2O_4$. Between 65 K and 20 K, a of LiV_2O_4 remains almost constant and then from 20 K down to 4 K it decreases again. This downturn below 20 K correlates with the crossover from

local moment magnetism to HF behaviour in LiV_2O_4 and reveals the strong coupling between the electronic and lattice degrees of freedom as the system crosses over to HF behaviour with decreasing T below T_K. Such decrease in a of LiV_2O_4 below 20 K contrasts strongly with the almost constant value of a of $LiTi_2O_4$ in the same temperature range. The evolution of other crystallographic parameters as a function of temperature is notably different between the two materials as well, and will be reported in detail elsewhere.

3. Concluding remarks

The lattice response to the crossover from the normal metallic paramagnetic to superconducting state in $LiTi_2O_4$ has been shown to be very different from the structural response to the crossover from the local moment to HF behaviour in LiV_2O_4. This work reveals also the strong coupling of subtle structural changes with the establishment of clearly distinct low-temperature behaviours in LiV_2O_4 and $LiTi_2O_4$. In this way, our results provide essential input for a theoretical framework that will explain the formation of HF behaviour of the $d^{1.5}$ compound LiV_2O_4, the mechanism of superconductivity in the $d^{0.5}$ compound $LiTi_2O_4$ and particularly why the properties of LiV_2O_4 are so divergent from those of $LiTi_2O_4$.

Acknowledgments

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