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Abstract
Metamagnetic behaviour has been observed in an LiV_2O_4 powder sample around 38 T at 4.2 K. On the other hand, the magnetization for oxygen deficient $LiV_2O_{3.92}$ shows no indication of metamagnetism up to 40 T, and shows substantially reduced magnetic moment compared to that of LiV_2O_4. These results suggest that ferromagnetic interaction is strongly enhanced by magnetic fields in LiV_2O_4, whereas antiferromagnetic interaction is dominant in $LiV_2O_{3.92}$.

1. Introduction

Recently, research on the spinel compound LiV_2O_4 has been an exciting field since the discovery of the large electronic specific heat coefficient $\gamma = 420$ mJ mol^{-1} K^{-2} at low temperature [1]. This value of γ is the largest among d-electron compounds. Moreover, LiV_2O_4 has been found to exhibit heavy-fermion-like behaviour, i.e., a broad maximum in the magnetic susceptibility χ [1–3], T^2-dependence in the electrical resistivity [4] and the Korringa type relaxation, $1/T_1 \propto T$, where $1/T_1$ is the spin–lattice relaxation rate derived from the ^7Li NMR measurements [1, 5, 6]. It should also be noted that the solid solution $Li_{1-x}Zn_xV_2O_4$ undergoes a metal–insulator transition as a function of x [2, 7, 8]. In spite of extensive studies, however, the origin of these anomalous behaviours has not been clearly established.

Several models have been proposed to explain the physical properties of LiV_2O_4. At first, the large γ was attributed to the Kondo-lattice formation as in the case of f-electron based compounds [1]. Mahajan *et al* have shown that their ^7Li NMR results are consistent with this mechanism. However, the temperature dependence of the electrical resistivity at high temperatures differs qualitatively from that of the f-electron based Kondo-lattice systems [4]. For the Kondo-lattice formation in LiV_2O_4, both the conduction and the localized electrons are

needed, whereas the presence of well defined localized electrons is not clearly demonstrated. On the other hand, Fujiwara *et al* [5] have interpreted their ^{7}Li NMR results as the characteristic behaviour of itinerant-electron systems with strongly enhanced ferromagnetic (FM) spin fluctuations. They have shown that the temperature dependence of $1/T_1$ is well described by the spin-fluctuation theory (SCR theory) for weakly or nearly FM metals [5]. Neutron scattering studies by Krimmel *et al* [9] have also suggested a possible nearly FM state for LiV_2O_4 at high temperatures. Thus, physical properties of LiV_2O_4 have been argued in terms of completely different electronic states, i.e., localized- or itinerant-electron systems. In addition, the effect of geometrical frustration arising from the spinel structure is suggested to be essential for the anomalous behaviour in LiV_2O_4 [4, 10]. This is inferred from the observations of spin-glass order in a slightly Mg- or Zn-doped variant [2–4].

To obtain further insight into the magnetic state of LiV_2O_4, we have performed a high-field magnetization measurement on LiV_2O_4. Since magnetic field can enhance the FM spin correlation, this experiment would give valuable information about the spin correlation in LiV_2O_4. To see the effect of geometrical frustration, we have also studied an oxygen-deficient sample $LiV_2O_{3.92}$.

2. Experimental details

A powder sample of LiV_2O_4 was prepared by a solid state reaction from powder samples of Li_3VO_4, V_2O_3 and V_2O_5. The same procedure as reported in [11] was employed. An oxygen-deficient sample $LiV_2O_{3.92}$ was prepared by varying the nominal composition. X-ray diffraction confirmed the spinel structure for both the samples. Magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) magnetometer at 1 kOe. High-field magnetization measurements were performed at 4.2 K by an induction method with well balanced pick-up coils. Magnetic fields up to 45 T were generated by a long-pulse magnet at the Institute for Solid State Physics, University of Tokyo.

3. Results

Figure 1 shows the inverse magnetic susceptibilities $1/\chi$ of LiV_2O_4 and $LiV_2O_{3.92}$ as functions of temperature T. For both the systems, χ follows a Curie–Weiss behaviour at high temperatures, and shows no evidence of magnetic ordering down to 2 K. $1/\chi$ of LiV_2O_4 shows a saturation behaviour around 10 K, and slightly decreases below 5 K. This small decrease is attributed to the contribution of impurities and/or defects. Subtracting a Curie term from this contribution yields a minimum at $T_m = 16$ K, as can be seen in the dotted curve in figure 1. This is consistent with those reported by several authors [1–3].

$1/\chi$ of $LiV_2O_{3.92}$ also shows a Curie–Weiss behaviour, and the data above 60 K agree with those of LiV_2O_4. Below about 20 K, $1/\chi$ of $LiV_2O_{3.92}$ decreases rapidly without any anomaly. The absence of an anomaly in χ of $LiV_2O_{3.92}$ has been suggested previously [2]. One may consider that a large contribution from defects masks a minimum in the intrinsic $1/\chi$ of $LiV_2O_{3.92}$. However, we found that a minimum is not given in $1/\chi$ of $LiV_2O_{3.92}$ by reasonable corrections. This suggests that χ of $LiV_2O_{3.92}$ at low temperature is qualitatively different from that of LiV_2O_4, though the high-temperature behaviours agree with each other.

Figure 2 shows magnetizations M of LiV_2O_4 and $LiV_2O_{3.92}$ as functions of magnetic field H. For both the systems, M increases linearly up to 15 T. At higher fields, M of LiV_2O_4 begins to increase nonlinearly, and exhibits an inflection point at $H_m = 38$ T. Such a metamagnetic behaviour in LiV_2O_4 is also reported in the literature [12]. The magnetic moment at 45 T is about 1.1 μ_B per formula unit (fu). In contrast, M of $LiV_2O_{3.92}$ increases monotonically up
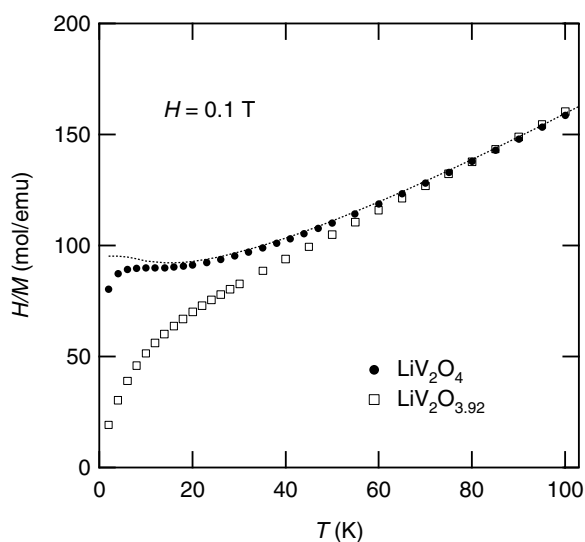
Figure 1. The inverse of the magnetic susceptibility $1/\chi$ of LiV$_2$O$_4$ and LiV$_2$O$_{3.92}$ powder samples. The dotted curve represents the corrected data of LiV$_2$O$_4$ with the Curie term subtracted.
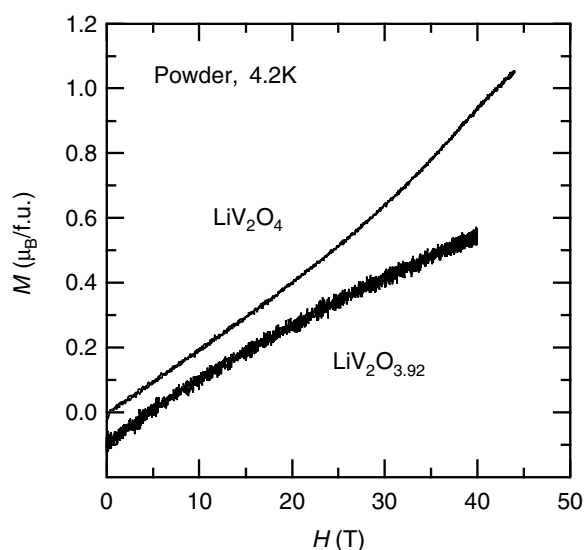

Figure 2. High-field magnetization M of LiV$_2$O$_4$ and LiV$_2$O$_{3.92}$ powder samples at 4.2 K. M of LiV$_2$O$_{3.92}$ is shifted by -0.1 μ_B for clarity.

to 40 T with no indication of metamagnetic behaviour. The value of M at 40 T is less than 0.7 μ_B/fu, considerably smaller than that of LiV$_2$O$_4$.

Figure 3 shows the Arrott plot of the two systems. The slope of M^2 versus H/M for LiV$_2$O$_4$ is negative, consistent with the metamagnetic behaviour. On the other hand, the slope for LiV$_2$O$_{3.92}$ is positive, in a clear contrast to that for LiV$_2$O$_4$. One can therefore expect that M of LiV$_2$O$_{3.92}$ increases monotonically until its saturation value, without metamagnetic behaviour even for much higher fields.
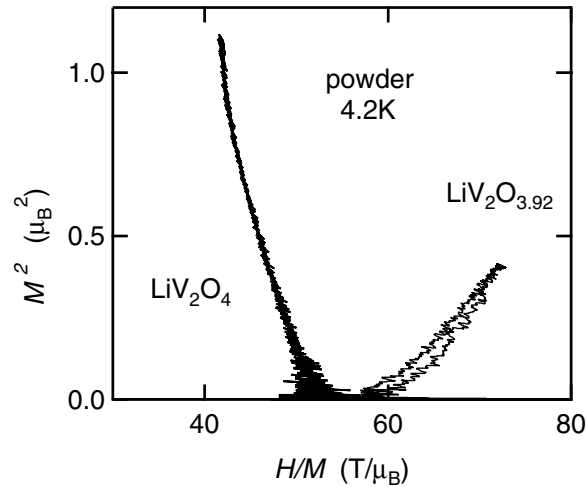
Figure 3. Arrot plot for LiV_2O_4 and $LiV_2O_{3.92}$ at 4.2 K.

4. Discussion

In this section, we argue about the possible mechanism for the metamagnetic behaviour in LiV_2O_4. Metamagnetic behaviour is usually explained as a spin-flopping process in antiferromagnetic (AFM) ordered systems. In contrast, LiV_2O_4 does not order magnetically down to the lowest temperature, as is demonstrated by many works including specific heat [1, 13, 14], ^7Li NMR [1, 2, 5, 6, 14], muon spin relaxation [1, 15] and neutron diffraction [16]. Hence, the metamagnetic behaviour observed in LiV_2O_4 is not attributed to a spin flopping. Alternatively, metamagnetic behaviour out of a paramagnetic state has been observed in such cases as

(i) Kondo-lattice systems like $CeRu_2Si_2$ [17], $CeCu_6$ [18, 19] or YbCuAl [20], and
(ii) itinerant-electron systems close to FM order [21] like YCo_2 [22] or $TiBe_2$ [23].

Notably, both the two models, Kondo lattice and nearly FM metal, have been used to explain the anomalous physical properties of LiV_2O_4.

For Kondo-lattice systems, the precise mechanism of the metamagnetic behaviour has not been clearly understood yet. Nevertheless, it is widely accepted that the metamagnetic behaviour accompanies a qualitative change in the f-electron state. For $CeRu_2Si_2$, where a distinct metamagnetic behaviour has been observed at $H_m = 7$ T [17], a drastic change in the magnetic response has been demonstrated by the neutron scattering studies [24]; from strong AFM fluctuations at $H < H_m$ to single-site (q-independent) fluctuations at $H > H_m$. A similar change in the magnetic response has also been observed in $CeCu_6$ [24]. Furthermore, the de Haas–van Alphen effect measurements on $CeRu_2Si_2$ have revealed the change in its Fermi surface from itinerant at low fields to almost localized f electrons at high fields [25]. Hence, the high-field states in these compounds are well described by localized f electrons with single-site Kondo fluctuations. It is also notable that the magnetization of $Ce_{1-x}(La, Y)_xRu_2Si_2$ at high fields is almost independent of x, though the metamagnetic behaviour becomes broadened with increasing x [26]. Similar behaviour is also observed in $Ce_{1-x}La_xFe_2Ge_2$ [27] and $Yb_{1-x}Y_xCuAl$ [28]. This substitution dependence is well explained by the single-site character of f electrons at high fields, since the single-site interactions are insensitive to disorder. Thus,

we can conclude that such a localized-electron state at high fields is a common feature in Kondo-lattice systems.

Here, note the qualitative difference in the magnetization of LiV$_2$O$_4$ and LiV$_2$O$_{3.92}$: M of LiV$_2$O$_{3.92}$ at 40 T is considerably smaller than that of LiV$_2$O$_4$. This distinct difference in M does not agree with the high-field state expected for Kondo-lattice systems. Therefore, the Kondo-lattice model is unlikely for LiV$_2$O$_4$ as far as the mechanism of the metamagnetic behaviour is concerned. Instead, this result is likely to suggest that the intersite correlation is still important even at high fields, because intersite correlation should be sensitive to disorder or defects. This indicates that the metamagnetic behaviour is relevant to the evolution of intersite FM correlation. Thus, we turn to the next picture; itinerant-electron systems close to FM order.

Within the itinerant-electron description, the Curie–Weiss susceptibility in LiV$_2$O$_4$ is attributed to the temperature dependent FM ($q \sim 0$) spin fluctuations, not to localized moments [29]. Here, Curie constants do not necessarily agree with the effective magnetic moment expected for a free ion, and a negative Weiss temperature no longer indicates AFM interactions. Several nearly FM metals exhibit metamagnetic behaviour as well as a maximum in χ [21]. Examples are YCo$_2$ [22], TiBe$_2$ [23] and Co(S, Se)$_2$ [30]. Recently, metamagnetic behaviour has also been reported in the metallic oxide Sr$_3$Ru$_2$O$_7$ around $H = 5$ T [31]. It is notable that this compound shows a maximum in χ and a large $\gamma \sim 100$ mJ Ru-mol^{-1} K^{-2}, and is considered to be close to an FM ordering [32]. These features of nearly FM metals are quite similar to those observed in LiV$_2$O$_4$ including the metamagnetic behaviour.

On the other hand, it has been shown that LiV$_2$O$_4$ also exhibits quite contrasting behaviour to the feature for nearly FM metals. For example, neutron scattering experiments by Lee *et al* have revealed the presence of AFM fluctuations at $Q \sim 0.6$ Å^{-1} [33]. In addition, spin-glass ordering has been observed in Mg- or Zn-doped samples [2–4]. These observations suggest the presence of strong AFM interaction and the effect of the geometrical frustration, the latter of which prevents this system from long-range AFM ordering. In this respect, LiV$_2$O$_4$ has been compared with (Y, Sc)Mn$_2$ and β-Mn [10], where the AFM order is suppressed by the geometrical frustration, and the resulting fluctuations enhance the electronic specific heat coefficients [34–36].

It should, however, be stressed that the temperature dependence of χ of (Y, Sc)Mn$_2$ and β-Mn differs qualitatively from that of LiV$_2$O$_4$. χ of the former are almost T independent and do not show Curie–Weiss behaviour [34, 35], consistent with the dominant AFM ($q \gg 0$) fluctuations. In contrast, χ as well as the ^{7}Li Knight shift K of LiV$_2$O$_4$ show Curie–Weiss behaviour, suggesting the importance of the FM ($q \sim 0$) fluctuation. Furthermore, the metamagnetic behaviour observed in the present study evidences the importance of the FM interaction in this system. From these facts, we conclude that both the FM ($q \sim 0$) and the AFM ($Q \sim 0.6$ Å^{-1}) interactions are important in LiV$_2$O$_4$. This is similar to the case in V$_5$Se$_8$, where both FM ($q \sim 0$) and AFM ($q \sim Q$) fluctuations are considered to be enhanced [37]. This model has successfully explained the itinerant AFM behaviour and the Curie–Weiss susceptibility of V$_5$Se$_8$ [37].

The presence of two kinds of spin-fluctuation in LiV$_2$O$_4$ has been suggested by the earlier neutron scattering study [9] and the SCR analysis for the specific heat data [14]. Recently, Eyert *et al* have performed first-principles calculations, and have shown that the AFM state is stable for LiV$_2$O$_4$ and the energy of the FM state is slightly higher [38]. This result is indicative that applying high fields would reduce the energy for the FM state, which results in a metamagnetic transition.

It is notable that the temperature where χ has a maximum is $T_{max} \simeq 10$ K for TiBe$_2$ [39] and $T_{max} = 16$ K for Sr$_3$Ru$_2$O$_7$ [32], comparable to $T_{max} = 16$ K for LiV$_2$O$_4$, whereas the

field where metamagnetic behaviour occurs is $H_m = 6$ T for TiBe$_2$ [23] and $H_m = 5$ T for Sr$_3$Ru$_2$O$_7$ [31], remarkably smaller than $H_m \simeq 38$ T for LiV$_2$O$_4$. This may be a result of competition of the FM and the AFM fluctuations in LiV$_2$O$_4$ below H_m. We expect that the AFM fluctuations are suppressed at around H_m and the FM correlation becomes dominant above H_m. On the other hand, FM correlation does not appear to develop in LiV$_2$O$_{3.92}$. This suggests that the AFM interaction is dominant even at high fields in this system.

Instead of the itinerant-electron picture mentioned above, the possibility of LiV$_2$O$_4$ as a localized-moment system is still not ruled out. The value of the spin–lattice relaxation rate $1/T_1$ of the ^{51}V [2] and of the ^{7}Li nuclei [6] at high temperatures are consistent with those for a localized-moment system. The evolution of localized electrons has been suggested theoretically by the splitting of the t$_{2g}$ orbital into almost localized A$_{1g}$ and conductive E$_g$ orbitals due to a trigonal distortion in the VO$_6$ octahedra and the Coulomb interactions [40]. In this case, the most probable explanation for the metamagnetic behaviour is the evolution of FM interaction due to the double exchange mechanism. Here, the FM interaction evolves via the Hund coupling between local moments and conduction electrons, while AFM interaction can also arise via the exchange interaction between local moments [2, 10, 40]. This would also result in the situation where both the FM and the AFM interactions are important.

Although our results do not clarify whether the d-electron state in LiV$_2$O$_4$ is itinerant or localized, the absence of metamagnetic behaviour in LiV$_2$O$_{3.92}$ seems to be of particular importance. The reduced M in this system implies that the FM interaction is rapidly reduced by a slight disorder or defects. This may be a hint at the origin of the FM interaction in LiV$_2$O$_4$. Since the d electrons in LiV$_2$O$_4$ involve degrees of freedom of orbital and charge quanta, orbital and/or charge order would also be suppressed by the geometrical frustration. This multiply frustrated state can be easily lifted by a small defect. The FM correlation in LiV$_2$O$_4$ may be a result of the competition of the multiply frustrated state. To elucidate the electronic state and the mechanism for the evolution of the FM correlation in LiV$_2$O$_4$, more systematic experiments as well as theoretical studies should be performed.

5. Conclusion

We have reported a metamagnetic behaviour in LiV$_2$O$_4$ around $H_m = 38$ T and the absence of metamagnetism in LiV$_2$O$_{3.92}$ up to 40 T. The Arrot plot of the former shows the characteristic curve for a metamagnetic behaviour, while that for the latter has a positive curve. This implies that metamagnetic behaviour would not appear for LiV$_2$O$_{3.92}$ even at much higher fields. Moreover, the high-field magnetic moment of this system is significantly smaller than that of LiV$_2$O$_4$. This qualitative difference in the magnetization of the two samples is of particular importance to considering the mechanism of the metamagnetic behaviour.

Metamagnetic behaviour out of a paramagnetic state has been observed in two cases: Kondo-lattice systems and itinerant-electron systems with strong FM spin fluctuations. For the case of Kondo-lattice systems, the high-field state is described by localized electrons with single-site Kondo fluctuations. Consequently, the magnetic moments at high fields are insensitive to a slight disorder or defects for Kondo-lattice systems. For the present case, the significant difference in the magnetization of LiV$_2$O$_4$ and LiV$_2$O$_{3.92}$ does not agree with the local moment state. The Kondo-lattice model is therefore unlikely as far as the mechanism for the metamagnetic behaviour is concerned. Instead, these results favour the evolution of intersite FM spin correlation at high fields for the origin of metamagnetic behaviour in LiV$_2$O$_4$.

This may lead to the interpretation that LiV$_2$O$_4$ is a nearly FM metal, as suggested by Fujiwara *et al* from their ^{7}Li NMR experiments [5]. In fact, many itinerant-electron systems with strong FM spin fluctuations exhibit metamagnetic behaviour in fields [21]. For LiV$_2$O$_4$,

however, neutron scattering experiments have revealed the presence of AFM fluctuations at low temperature [33]. From these facts, we conclude that both the FM and the AFM interactions are important in LiV$_2$O$_4$, and the former is strongly enhanced by external fields.

The microscopic origin of the FM correlation is unclear. The qualitative difference in the high-field magnetizations of LiV$_2$O$_4$ and LiV$_2$O$_{3.92}$ is likely to suggest that the effect of geometrical frustration for spin, orbital and charge order is relevant to the FM interaction. The other possibility for the FM correlation would be the double exchange mechanism.

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