High-field magnetization of the 3d heavy-fermion system LiV$_{2}$O$_{4-\delta}$ ($\delta = 0, 0.08$)

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Abstract. Metamagnetic behavior has been observed in LiV$_{2}$O$_{4}$ powder sample around 38 T at 4.2 K. On the other hand, magnetization for oxygen deficient LiV$_{2}$O$_{3.92}$ shows no indication of metamagnetism up to 40 T, and shows substantially reduced magnetic moment compared to that of LiV$_{2}$O$_{4}$. These results suggest that ferromagnetic interaction is strongly enhanced by magnetic fields in LiV$_{2}$O$_{4}$, whereas antiferromagnetic interaction is dominant in LiV$_{2}$O$_{3.92}$.

PACS numbers: 71.27.+a, 75.40.Cx, 75.90.+w

Submitted to: J. Phys.: Condens. Matter
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1. Introduction

Recently, research on the spinel compound LiV$_{2}$O$_{4}$ has been an exciting field since the discovery of the large electronic specific heat coefficient $\gamma = 420$ mJ/mol$\cdot$K$^{2}$ at low temperature [1]. This value of $\gamma$ is the largest among $d$-electron compounds. Moreover, LiV$_{2}$O$_{4}$ has been found to exhibit heavy-fermion like behavior; i.e., a broad maximum in the magnetic susceptibility $\chi$ [1, 2, 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 $^{7}$Li-NMR measurements [1, 5, 6]. It should also be noted that the solid-solution Li$_{1-x}$Zn$_{x}$V$_{2}$O$_{4}$ undergoes a metal-insulator transition as a function of $x$ [2, 4, 8]. In spite of enormous studies, however, origin of these anomalous behavior is not clearly solved.

Several models have been proposed to explain the physical properties of LiV$_{2}$O$_{4}$. At first, the large $\gamma$ has been attributed to the Kondo-lattice formation as in the case of $f$-electron based compounds [1]. Mahajan et al. have shown that their $^{7}$Li-NMR results are consistent with this mechanism. However, temperature dependence of the
electrical resistivity at high temperatures differs qualitatively from that of the \( f \)-electron based Kondo-lattice systems \[\text{[4]}\]. For the Kondo-lattice formation in LiV\(_2\)O\(_4\), 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 \textit{et al.} have interpreted their \( ^7\text{Li}\)-NMR results as the characteristic behavior of itinerant-electron systems with strongly-enhanced ferromagnetic spin-fluctuations \[\text{[5]}\]. 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-ferromagnetic metals \[\text{[5]}\]. Neutron scattering studies by Krimmel \textit{et al.} have also suggested possible nearly-ferromagnetic state for LiV\(_2\)O\(_4\) at high temperatures \[\text{[9]}\]. Thus, physical properties of LiV\(_2\)O\(_4\) 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 behavior in LiV\(_2\)O\(_4\) \[\text{[4, 10]}\]. This is inferred from the observations of spin-glass order in a slightly Mg- or Zn-doped variants \[\text{[2, 3, 4]}\].

To obtain further insight for the magnetic state of LiV\(_2\)O\(_4\), we have performed a high-field magnetization measurement on LiV\(_2\)O\(_4\). Since magnetic field can enhance the ferromagnetic spin-correlation, this experiment would give valuable information about the spin correlation in LiV\(_2\)O\(_4\). To see the effect of geometrical frustration, we have also studied on an oxygen-deficient sample LiV\(_2\)O\(_{3.92}\).

2. Experimental

Powder sample of LiV\(_2\)O\(_4\) was prepared by a solid state reaction from powder samples of Li\(_3\)VO\(_4\), V\(_2\)O\(_3\), and V\(_2\)O\(_5\). The same procedure reported in ref. \[\text{[11]}\] was employed. An oxygen deficient sample LiV\(_2\)O\(_{3.92}\) 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 pickup 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 inverse magnetic susceptibility \( 1/\chi \) of LiV\(_2\)O\(_4\) and LiV\(_2\)O\(_{3.92}\) as functions of temperature \( T \). For both the systems, \( \chi \) follows a Curie-Weiss behavior at high temperatures, and shows no evidence of magnetic ordering down to 2 K. \( 1/\chi \) of LiV\(_2\)O\(_4\) shows a saturation behavior around 10 K, and slightly decreases below 5 K. This small decrease is attributed to the contribution of impurities and/or defects. Subtracting this contribution by a Curie term yields a minimum at \( T_m = 16 \) K, as can be seen in the dotted line in Fig. 1. This is consistent with those reported by several authors \[\text{[4, 5, 6]}\]. \( 1/\chi \) of LiV\(_2\)O\(_{3.92}\) also shows a Curie-Weiss behavior, and the data above 60 K agree
High-field magnetization of LiV$_2$O$_4$ with those of LiV$_2$O$_{3.92}$. Below about 20 K, $1/\chi$ of LiV$_2$O$_{3.92}$ decreases rapidly without any anomaly. Absence of anomaly in $\chi$ of LiV$_2$O$_{3.92}$ has been suggested previously [2]. One may consider that a large contribution from defects masks a minimum in the intrinsic $1/\chi$ of LiV$_2$O$_{3.92}$. However, we found that a minimum is not given in $1/\chi$ of LiV$_2$O$_{3.92}$ by reasonable corrections. This suggests that $\chi$ of LiV$_2$O$_{3.92}$ at low temperature is qualitatively different from that of LiV$_2$O$_4$, though the high-temperature behavior agrees each other.

Figure 2 shows magnetization $M$ of LiV$_2$O$_4$ and LiV$_2$O$_{3.92}$ as functions of magnetic field $H$. For both the systems, $M$ increases linearly up to 15 T. At higher fields, $M$ of LiV$_2$O$_4$ turns to increase nonlinearly, and exhibits an inflection point at $H_m = 38$ T. Such a metamagnetic behavior in LiV$_2$O$_4$ is also reported in the literature [12]. Magnetic moment at 45 T is about 1.1 $\mu_B$ per formula unit (f.u.). In contrast, $M$ of LiV$_2$O$_{3.92}$ increases monotonically up to 40 T with no indication of metamagnetic behavior. The value of $M$ at 40 T is less than 0.7 $\mu_B$/f.u., considerably smaller than that of LiV$_2$O$_4$.

Figure 3 shows the Arrott-plot of the two systems. The slope of $M^2$ vs. $H/M$ for LiV$_2$O$_4$ is negative, consistent with the metamagnetic behavior. 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 behavior even for much higher fields.

4. Discussion

In this section, we argue on the possible mechanism for the metamagnetic behavior in LiV$_2$O$_4$. Metamagnetic behavior is usually explained as a spin-flopping process in antiferromagnetic (AFM) ordered systems. In contrast, LiV$_2$O$_4$ does not order magnetically down to the lowest temperature, as is demonstrated by many works including specific heat [1, 13, 14], $^7$Li-NMR [1, 2, 5, 6, 14], muon spin relaxation [1, 15] and neutron diffraction [16]. Hence, the metamagnetic behavior observed in LiV$_2$O$_4$ is not attributed to a spin-flopping. Alternatively, metamagnetic behavior out of a paramagnetic state has been observed in such cases as: (i) Kondo-lattice systems like CeRu$_2$Si$_2$ [17], CeCu$_6$ [18, 19] or YbCuAl [20], and (ii) itinerant-electron systems close to ferromagnetic (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$_2$O$_4$.

For Kondo-lattice systems, the precise mechanism of the metamagnetic behavior has not been clearly understood yet. Nevertheless, it is widely accepted that the metamagnetic behavior accompanies a qualitative change in the $f$-electron state. For CeRu$_2$Si$_2$, where a distinct metamagnetic behavior 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 $H > H_m$. Similar change in the magnetic response has also been observed in CeCu$_6$ [24]. Furthermore, the de Haas-van Alphen effect measurements
on CeRu$_2$Si$_2$ have revealed the change in its Fermi surface from itinerant at low fields to almost localized $f$-electrons at high fields \[23\]. 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)$_x$Ru$_2$Si$_2$ at high fields is almost independent of $x$, though the metamagnetic behavior becomes broadened with increasing $x$ \[26\]. Similar behavior is also observed in Ce$_{1-x}$La$_x$Fe$_2$Ge$_2$ \[27\] and Yb$_{1-x}$Y$_x$CuAl \[28\]. 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 behavior 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 behavior 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 antiferromagnetic (AFM) interactions. Several nearly-FM metals exhibit metamagnetic behavior as well as a maximum in $\chi$ \[21\]. Such examples are YCo$_2$ \[22\], TiBe$_2$ \[23\], and Co(S,Se)$_2$ \[30\]. Recently, metamagnetic behavior 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 $\chi$ and a large $\gamma \sim 100$ mJ/Ru-mol·K$^2$, and is considered to be close to a FM ordering \[12\]. These features of nearly-FM metals are quite similar to those observed in LiV$_2$O$_4$ including the metamagnetic behavior.

On the other hand, it has been shown that LiV$_2$O$_4$ also exhibits quite contrasting behavior 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 \[2, 3, 4\]. These observations suggest the presence of strong AFM interaction and the effect of the geometrical frustration, the latter of which prevents this system from a long-range AFM ordering. In this respect, LiV$_2$O$_4$ has been compared with (Y,Sc)Mn$_2$ and $\beta$-Mn \[10\], where the AFM order is suppressed by the geometrical frustration, and the resulting fluctuations enhance the electronic specific heat coefficients \[34, 35, 36\].

It should, however, be stressed that the temperature dependence of $\chi$ of (Y,Sc)Mn$_2$ and $\beta$-Mn differs qualitatively from that of LiV$_2$O$_4$. $\chi$ of the formers are almost $T$-independent and do not show Curie-Weiss behavior \[34, 35\], consistent with the
dominant AFM ($q \gg 0$) fluctuations. In contrast, $\chi$ as well as the $^7$Li-Knight shift $K$ of LiV$_2$O$_4$ show Curie Weiss behavior, suggesting the importance of the FM ($q \sim 0$) fluctuation. Furthermore, the metamagnetic behavior 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 ($Q \sim 0.6 \, \text{Å}^{-1}$) 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 behavior and the Curie-Weiss susceptibility of V$_5$Se$_8$ $^{37}$.

The presence of two kind of spin-fluctuations 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 AFM state is stable for LiV$_2$O$_4$ and the energy of 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 $\chi$ has a maximum is $T_{\text{max}} \approx 10 \, \text{K}$ for TiBe$_2$ $^{39}$ and $T_{\text{max}} = 16 \, \text{K}$ for Sr$_3$Ru$_2$O$_7$ $^{32}$, comparable to $T_{\text{max}} = 16 \, \text{K}$ for LiV$_2$O$_4$, whereas the field where metamagnetic behavior occurs is $H_m = 6 \, \text{T}$ for TiBe$_2$ $^{33}$ and $H_m = 5 \, \text{T}$ for Sr$_3$Ru$_2$O$_7$ $^{31}$, remarkably smaller than $H_m \approx 38 \, \text{T}$ 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 not still 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 trigonally distortion in the VO$_6$ octahedra and the Coulomb interactions $^{40}$. In this case, the most probable explanation for the metamagnetic behavior 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 behavior 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 for 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
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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 behavior in LiV$_2$O$_4$ around $H_m = 38$ T and absence of metamagnetism in LiV$_2$O$_{3.92}$ up to 40 T. Arrot plot of the former shows the characteristic curve for a metamagnetic behavior, while that for the latter has a positive curve. This implies that metamagnetic behavior would not appear for LiV$_2$O$_{3.92}$ even at much higher fields. Moreover, high-field magnetic moment of this system is significantly smaller from that of LiV$_2$O$_4$. This qualitative difference in the magnetization of the two samples is of particular importance to consider the mechanism of the metamagnetic behavior.

Metamagnetic behavior out of a paramagnetic state has been observed in two cases: Kondo-lattice systems and itinerant-electron systems with strong ferromagnetic 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 behavior is concerned. Instead, these results favor the evolution of intersite ferromagnetic spin-correlation at high fields for the origin of metamagnetic behavior in LiV$_2$O$_4$.

This may lead to the interpretation that LiV$_2$O$_4$ is a nearly-ferromagnetic metals, as is suggested by Fujiwara et al. from their $^7$Li-NMR experiments [5]. In fact, many itinerant-electron systems with strong ferromagnetic spin-fluctuations exhibit metamagnetic behavior by fields [21]. For LiV$_2$O$_4$, however, neutron scattering experiments have revealed the presence of antiferromagnetic fluctuations at low temperature [33]. From these facts, we conclude that both the ferromagnetic and the antiferromagnetic interactions are important in LiV$_2$O$_4$, and the former is strongly enhanced by external fields.

Microscopic origin of the ferromagnetic 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 ferromagnetic interaction. The other possibility for the ferromagnetic correlation would be the double exchange mechanism.

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Figure 1. Inverse of the magnetic susceptibility $1/\chi$ of LiV$_2$O$_4$ and LiV$_2$O$_{3.92}$ powder samples. Dotted line 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 $-0.1 \mu_B$ for clarity.

**Figure 3.** Arrot plot for LiV$_2$O$_4$ and LiV$_2$O$_{3.92}$ at 4.2 K.