Anomalous spin fluctuation in vanadium spinel LiV_2O_4 studied by ^{7}Li-NMR

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Nuclear magnetic resonance for ^{7}Li nuclei was performed in vanadium spinel, LiV_2O_4 from 4.2 K up to 760 K. An anomalous temperature dependence of the relaxation time T_1 was observed. Namely, the relaxation rate $1/T_1$ increases with increasing temperature and reaches a maximum around 50 K and then becomes nearly constant. Such an anomalous behavior was investigated from the viewpoint of the ferromagnetic instability predicted in the self-consistent-renormalization theory. [S0163-1829(98)05706-3]

I. INTRODUCTION

Vanadium spinel LiV_2O_4 has been investigated as an end material which has a metal-insulator transition upon substituting Zn for Li. Single crystal LiV_2O_4 had been synthesized by Roger *et al.* in 1964 and they have reported metal-like conductivity.[1] The powder samples are semiconductive and the order of the resistivity is 10^{-5} Ωm.[2] It has been reported that the metal-insulator transition occurs by substituting Zn 35% for Li from the Seebeck coefficient[2] and by substituting Zn 45% from the Seebeck coefficient and far infrared absorption.[3] Another interesting phenomenon in relation to Zn substitution is the appearance of spin-glass phase at low temperatures below 10 K.[4] The spin-glass phase appears in a wide region from Zn 20% to Zn 90%. It may safely be said that LiV_2O_4 locates nearby the spin-glass phase in the phase diagram. As is reported by many papers[4–6] the susceptibility shows Curie-Weiss behavior, $\chi=\chi_0+\chi_d$, where χ_0 is a constant and χ_d represents the Curie-Weiss low. The effective moment per V site is nearly $S=\frac{1}{2}$. The Weiss constant is about -33 K and χ_0 is 2.3×10^{-4} emu/mol. Recently, quite large specific-heat coefficient $\gamma\sim420$ mJ/mol K^2 has been reported by Kondo *et al.*,[7] whereas Fujimori *et al.* have observed low density of state near the Fermi energy from photoemission experiments and suggested the coexistence of d^1 and d^2 configurations in the experimental time scale ($\sim10^{-15}$ sec^{-1}).[8] LiV_2O_4 includes many anomalous features as a strongly correlated electron system.

In the present work, we have performed nuclear magnetic resonance (NMR) for ^{7}Li in pure LiV_2O_4 up to 760 K and analyzed from the viewpoint of the self-consistent renormalization (SCR) theory near ferromagnetic instability.[9] We have also investigated the susceptibility and the specific-heat coefficient in the frame of the SCR theory.

II. EXPERIMENTAL RESULTS

A. Knight shift

NMR spectra for ^{7}Li are free from electric quadrupole interaction since Li locates on the center of tetrahedra of the oxygen. A narrow NMR line below 30 G was observed in the NMR spectra. This implies that there appear no phase transitions and magnetic orders in the relevant temperature range.

The temperature dependence of the Knight shift up to 700 K is shown in Fig. 1. The data below 300 K have been already reported in Ref. 10. The value of the shift becomes the maximum around 20 K and then decreases with increasing temperature. Such a maximum also appears in the static susceptibility around 20 K. The static susceptibility data up to 700 K are shown in Fig. 2. The shift originates from transferred hyperfine interaction between nucleus and *d* electrons, and is related to the temperature dependent part of the susceptibility χ_d as $K\propto A_{\rm tr}\chi_d z_{\rm Li}$, where $A_{\rm tr}$ is the transferred hyperfine coupling constant and $z_{\rm Li}(=12)$ is the number of the nearest neighbor V ions. The value of $A_{\rm tr}$ is obtained as 0.18 kOe/μ_β from the K-χ plot in Fig. 3. The effective coupling constant $A_{\rm hf}$ per ^{7}Li nucleus is given as $A_{\rm hf}^2=z_{\rm Li}A_{\rm tr}^2+A_{\rm dip}^2$, where $A_{\rm dip}$ represents dipolar coupling. The dipolar coupling is calculated as 0.66 kOe/μ_β by neglecting the correlation between V ions. Then, the value of $A_{\rm hf}$ is obtained as 0.91 kOe/μ_β.

B. Relaxation rate $1/T_1$

Spin-lattice relaxation time T_1 was measured for ^{7}Li by usual pulse saturation recovery method at the field 1.0 T. The recovery curve shows single exponential decay over two orders of magnitude. The temperature dependence of the spin-lattice relaxation rate $1/T_1$ up to 760 K is shown in Fig. 4. There appears the maximum at about 50 K that is larger than that of the susceptibility or the shift. The maximum does not correspond to any magnetic transitions nor crystallographic phase transitions, as is mentioned above. The rate $1/T_1$ seems to approach to a constant value ($1/T_1\sim17$ sec^{-1}), although a slight increase is seen above 600 K.

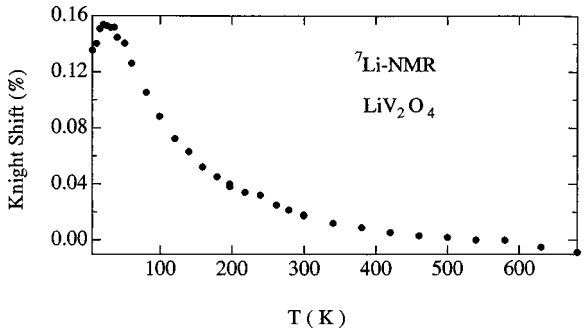

FIG. 1. Temperature dependence of the Knight shift for ^{7}Li up to 700 K.

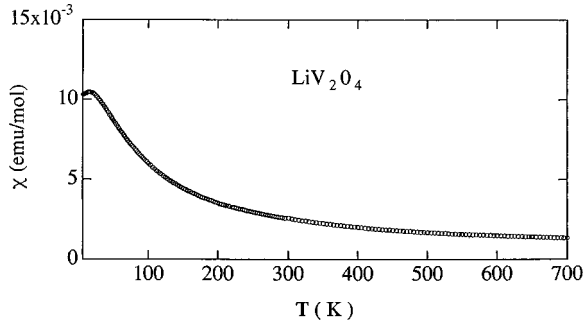

FIG. 2. Temperature dependence of the static susceptibility up to 700 K.

The behavior that $1/T_1$ approaches a constant and that the susceptibility obeys the Curie-Weiss low is seen in the following three cases. The first is nearly or weakly ferromagnetic metals such as $ZrZn_2$ (Ref. 11) where the q-dependent susceptibility χ_q is enhanced only for small q and the average amplitude of the local spin fluctuation $\langle S_L{}^2\rangle$ is proportional to temperature. The second is metallic localized moment system such as Mn Heusler alloys In_2MnGa (Ref. 12) where χ_q is almost q-independent and $\langle S_L{}^2\rangle = S(S+1)$. The third is temperature induced local moment system such as CoSe (Ref. 13) or CoTi (Ref. 14) where $\langle S_L{}^2\rangle$ increases with increasing temperature and approaches to a constant at high temperatures. It may be pointed out that the present compound would belong to the metallic localized moment system since the Curie constant is quite large. In this case $1/T_1$ becomes a constant at high temperatures and is given as $1/T_1 = \sqrt{2\pi}(A/\hbar)^2 S(S+1)/3\omega_e$, where the hyperfine coupling $A/\hbar$ is 1.9×10^7 $\sec^{-1}$, and the exchange frequency ω_e is $\sqrt{8J^2zS(S+1)/3}$, respectively. The values of the exchange coupling J and the number of the nearest neighbors z are 10 K and 6, respectively. Then, $1/T_1$ is calculated as 49.6 $\sec^{-1}$, which is almost three times larger than the experimental results. Moreover, the relation, $1/T_1 =$ constant should be held in the wide temperature range since the value of J is quite small ($\sim$10 K). Therefore, the experimental results are not accounted by the metallic localized moment system. The experimental results of $1/T_1$ including the anomaly around 50 K should be explained throughout the whole temperature range.

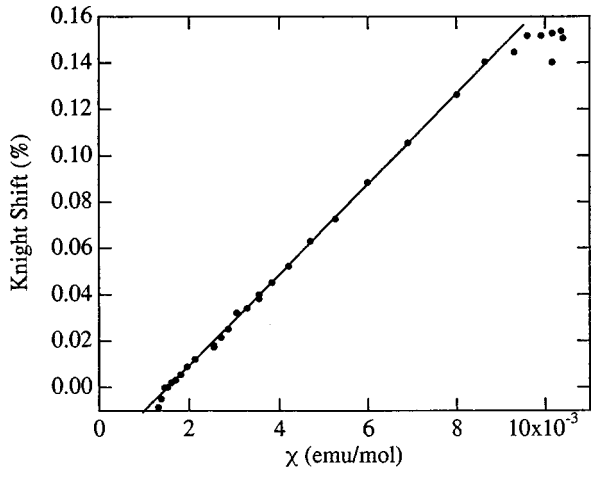

FIG. 3. K-χ plot for ^{7}Li in LiV_2O_4.

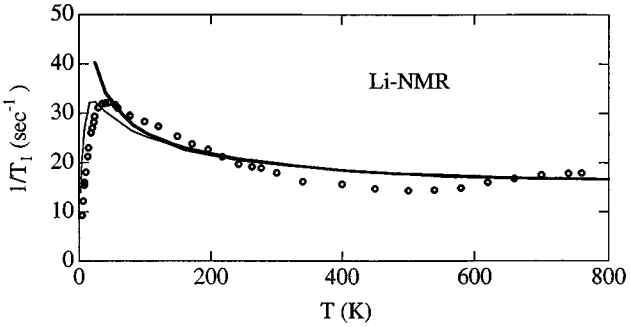

FIG. 4. Temperature dependence of $1/T_1$ for ^{7}Li up to 760 K. Solid curves represent the calculation based on the SCR theory nearby the ferromagnetic instability. The bold curve represents the calculation for $y_0 = 0$ in Eqs. (3), (4), and (5), and the other curve for $y_0 = 6\times10^{-5}$.

We examine, from now on, the origin of the anomaly from the viewpoint of the ferromagnetic instability which has been theoretically investigated by Ishigaki and Moriya[9] on the basis of the SCR theory. In the present compound, the origin that gives rise to the ferromagnetic instability would be the critical location in the phase diagram of $(Li_{1-x}Zn_x)V_2O_4$. Although the pure LiV_2O_4 is paramagnetic, it locates on the critical region nearby the phase boundary for the spin-glass phase.

III. ANALYSIS

The rate $1/T_1$ due to electronic spin fluctuation is generally given by using dynamical susceptibility $\chi^{-+}(q,\omega)$ as

$$1/T_1 = \hbar\gamma_N{}^2 T/N_A \Sigma_q |A_q|^2 \mathrm{Im}\chi^{-+}(Q+q,\omega_N)/\omega_N, \quad (1)$$

where γ_N, A_q, N_A, and Q are gyromagnetic ratio, the Fourier q component of the hyperfine coupling constant, number of the ions, and the magnetic ordering vector, respectively. In the present case $Q=0$. According to the SCR theory for ferromagnets, $\chi(q,\omega)$ is given as

$$\chi(q,\omega) = \frac{T_0}{2T_A}\frac{x}{T_0 x(y+x^2) - i\omega}, \quad (2)$$

where $x = q/(6\pi^2/v_0)^{1/3}$ and $y = 1/2T_A\chi$, respectively. T_A and T_0 characterize the energy width and the width of the distribution of the static susceptibility in the q space, respectively. Then, $1/T_1$ is obtained from Eq. (1) and (2) as,[9]

$$\frac{1}{T_1} = \frac{3\hbar\gamma_N{}^2}{4\pi}\frac{A_{\mathrm{hf}}{}^2}{T_A}\frac{t}{y}, \quad (3)$$

where

$$t = T/T_0, \quad y = y_0 + \frac{3}{2}y_1\int_0^1 dx x^3\left[\ln u - \frac{1}{2u} - \psi(u)\right], \quad (4)$$

$$u = x(y+x^2)/t, \text{ and } y_0 = 1/2T_A\chi(T=0), \quad (5)$$

respectively. The function $\psi(u)$ appearing in Eq. (4) is digamma function. The physical meaning of y_0 is a measure of distance from the phase boundary and is inversely proportional to the exchange enhancement factor. The effect of y_0

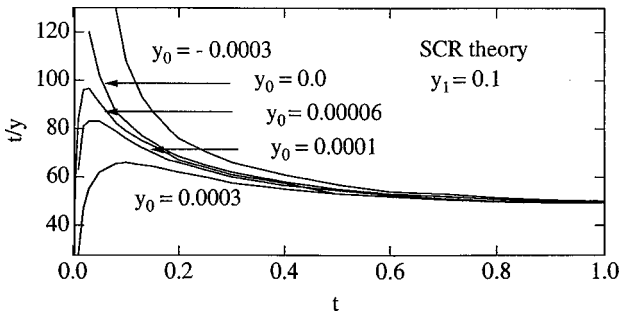

FIG. 5. The calculation of the temperature dependence of $t/y \propto (1/T_1)$ on the basis of the SCR theory.

on the inverse susceptibility, ($\propto y$) appears mainly at low temperatures and does not affect at high temperatures. The temperature dependence of $1/T_1$ qualitatively depends on the value of y_0. Typical temperature dependence of $1/T_1$ for several values of y_0 is shown in Fig. 5. The ferromagnetic order is seen in the region $y_0<0$. In this region $1/T_1$ diverges with decreasing temperature towards the ferromagnetic order. On the other hand, the region $y_0>0$ corresponds to a paramagnetic phase. The rate $1/T_1$ shows the T linear dependence at low temperatures and then approaches to a constant at high temperatures for fairly large value of y_0, whereas $1/T_1$ shows the T linear dependence and takes the maximum at some temperatures, and then decreases towards a constant with increasing temperature for quite small y_0. At phase boundary $y_0=0$, $1/T_1$ shows $T^{-1/3}$ dependence.[9]

The parameters required for the SCR theory are y_0, y_1, T_0, and T_A. In the present work, we can estimate T_0 from the temperature dependence of $1/T_1$. The value of T_0 is estimated as about 800 K from $1/T_1$ for $y_0=0$ in the temperature range between 50 and 760 K. The rate in Eq. (3) is calculated by using $A_{\rm hf}=0.91$ kOe/μ_B as,

$$1/T_1=6.57\times10^2 t/yT_A \quad (\sec^{-1}). \tag{6}$$

The temperature dependence of $1/T_1$ quite weakly depends on the values of y_1 between $y_1=1$ and 0.01. The value of y_1 is assumed as 0.1 guessing from the value of $ZrZn_2$. The parameter T_A is determined from $1/T_1$ at high-temperature limit if y_1 is fixed to a value. The value of T_A is obtained as 2 000 K by using $y_1=0.1$ and $1/T_1=17\ \sec^{-1}$ at high-temperature limit. The decrease of $1/T_1$ observed in the experiment at low temperatures below 50 K would be attributed to the existence of small y_0 in the frame of the SCR theory. The small y_0 is also necessary to suppress the divergence of the susceptibility. The value of y_0 is roughly estimated as 6×10^{-5} from $1/T_1$ at low temperatures. The calculated curves for $y_0=0$ and $y_0=6\times10^{-5}$ are shown by the solid curves in Fig. 4. The anomalous feature of $1/T_1$ in this compound is essentially attributed to the critical phenomenon near the phase boundary.

IV. DISCUSSION

Next, we discuss the specific-heat coefficient and the susceptibility in the frame of the theory and discuss the possibility of other relaxation mechanisms in this section.

A. Specific-heat coefficient

The large γ about 420 mJ/mol K^2 has been reported in this compound as is mentioned in the Sec. I. The heavy Fermi-liquid behavior has been pointed out from the temperature dependence of γ as well as the large value of γ. However, the origin which gives rise to the similarity with heavy fermion system is still open question. The specific heat around the ferromagnetic instability has also been calculated by Ishigaki and Moriya.[15] The temperature dependence of γ just at $y_0=0$ is proportional to $-\ln T$. $\gamma(T)$ is calculated for small y_0 at quite low temperatures ($t\ll y_0 \ll 1$) as,

$$\gamma(T)\sim\frac{3Nk_B}{2T}\int_0^1 dx\,\frac{x^2}{u} \tag{7}$$

$$=-\frac{3Nk_B}{4T_0}\ln\left(y_0+\frac{y_1t^2}{16y_0}\right), \tag{8}$$

where N represents the number of vanadium ions per mole. Therefore, $\gamma(0)$ is given as

$$\gamma(0)=-\frac{3Nk_B}{4T_0}\ln y_0. \tag{9}$$

As is seen from Eq. (9), $\gamma(0)$ is related with the inverse susceptibility, and the value becomes large in the ferromagnetically instable region. If $y_0=6\times10^{-5}$ and $T_0=800$ K are assumed for instance, $\gamma(0)$ becomes 150 mJ/mol K^2. This value is about one third of the experimental result. The fact that the calculated value becomes the same order with the experimental value suggests that the origin of the large $\gamma(0)$ is essentially magnetic one.

B. Susceptibility

The susceptibility is represented on the basis of the theory as

$$\chi=N(g\mu_B)^2/2k_BT_Ay \tag{10}$$

$$=1.5/T_Ay \quad (\text{emu/mol}). \tag{11}$$

The temperature dependence of χ is determined from Eq. (4). At high temperatures, y is proportional to T, then χ shows Curie-like behavior. The value of T_A should be taken as 8.0×10^4 K to fit the experimental results and this value is about one order larger than that obtained from the analysis of $1/T_1$. The deviation may originate from the q ($\neq0$) dependence of $\chi(q)$, since the susceptibility is free from the q dependence of $\chi(q)$. The contribution to $1/T_1$ of spin fluctuation other than $q=0$ would exist in this material. As a reason of the deviation, there lies the background that the ground state of the ordered phase for Zn doped samples is not the ferromagnetic state but the spin glass.

However, the maximum of $1/T_1$ around 50 K is considered characteristic of the ferromagnetic instability, although the spin fluctuation from $q\neq0$ is not neglected. $1/T_1$ around the antiferromagnetic instability has also been calculated by Ishigaki and Moriya.[9] The results of $1/T_1$ exhibit monotonous temperature dependence and no anomaly corresponding to the maximum of $1/T_1$.

The ferromagnetic spin fluctuation would be the main contribution to the Curie-Weiss behavior of the susceptibility as well as the anomalous behavior of $1/T_1$. However, the present compound is often treated as antiferromagnetic system since the susceptibility shows the Curie-Weiss behavior and the Weiss constant is negative (~ -30 K) in the viewpoint of the localized system. It is doubtful whether the system is antiferromagnetic as far as the results of $1/T_1$ are concerned. The investigation of the dynamical properties through T_1 measurement or inelastic neutron scattering is quite important to seek the nature of this system.

C. Comparison of $1/T_1$ with heavy fermion system

It should be noted that the temperature dependence of $1/T_1$ presented here looks like that of the heavy fermion system as well as the large $\gamma(T)$. It is likely that the maximum of $1/T_1$ appears in this case as a crossover of two relaxation mechanisms; one is due to conduction electrons which give rise to the Korringa relation at low temperatures and the other is due to localized f electrons that fluctuate by the elastic scattering with the conduction electrons. Two relaxation mechanisms appear in the damping factor Γ of $1/T_1$ ($\propto T\chi/\Gamma$) as $\Gamma=\Gamma_0+\Gamma_1 T$ ($\Gamma_0,\Gamma_1=$const). The second term of Γ represents the Korringa relation between the f electrons and the conduction electrons.

Such a relaxation mechanism would be possible if some of the d electrons in the t_{2g} state would play the role of the conduction electrons and the others the role of the localized electrons. It may be possible that mix valence state of d^1 and d^2 configuration is nearly realized by some orbital orders and that the valence fluctuation between them in space or time would occur. However, it seems impossible to consider different roles in the t_{2g} state. Thus, the process appearing in the heavy fermion system is not applicable in this system.

V. CONCLUSION

We have measured $1/T_1$ for ^{7}Li in LiV_2O_4 up to 760 K and the anomalous temperature dependence was investigated from the viewpoint of the ferromagnetic instability predicted by the SCR theory. Although quantitatively perfect agreement with the theory was not obtained, the primary features of $1/T_1$ were interpreted by the theory throughout the wide temperature range up to 760 K without introducing any other relaxation mechanisms. The anomaly of $1/T_1$ at about 50 K would be essentially the critical phenomenon near the phase boundary for the spin-glass phase appearing in the wide range of $Li_{1-x}Zn_xV_2O_4$ ($0.2\leqslant x\leqslant 0.9$).

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