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Li NMR in LiV_2O_4 under high pressure

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Abstract

The Knight shift K and the nuclear spin–lattice relaxation time T_1 of ^{7}Li have been measured under high pressure up to 4.74 GPa. $1/T_1T$ becomes larger on applying higher pressure below 10 K and does not obey the T_1T = constant relation down to 1 K. Meanwhile, K is independent of pressure above 2 GPa, indicating that the uniform component of the susceptibility does not change under high pressure. These results indicate that some antiferromagnetic fluctuations with wavevector $\mathbf{q} \neq 0$ dominate the relaxation rate in LiV_2O_4 near the boundary of the pressure induced insulating phase. It is noted that the pressure dependence of T_1 for LiV_2O_4 is opposite to that of typical Ce HF compounds, such as $CeCu_{5.9}Au_{0.1}$ and $CeCu_2Si_2$. At the highest pressure of 4.74 GPa, we found that $1/T_1$ obeys a power law dependence of $T^{2/3}$ over the wide T range between 60 mK and 10 K. The spin dynamics under high pressure will be discussed.

1. Introduction

Vanadium oxide LiV_2O_4 with a spinel structure was recently found to be the first example of a 3d-electron system with heavy fermion (HF) behaviour [1, 2]. The specific heat coefficient of $\gamma \approx 420$ mJ mol^{-1} K^{-2} at low temperature and the Wilson ratio of 1.7 are consistent with a Fermi liquid picture with a heavy mass [1]. The resistivity shows a metallic conductivity with the large coefficient A (=2.0 $\mu\Omega$ cm K^{-2}) of the T^2 term and the relation between γ and A has been confirmed to follow the Kadowaki–Woods plot in the f-electron system [2]. The nuclear spin–lattice relaxation rate $1/T_1$ shows a broad maximum around 50 K corresponding to localized spin fluctuation. However, $1/T_1$ obeys the Korringa relation ($R = K^2T_1T/S$) with the ratio $R \approx 0.7$ below 4 K [1, 3], which is also expected in the Fermi liquid picture, where K is the Knight shift and S is an inherent constant value of the observed nucleus. These results demonstrate a crossover from localized moment to Fermi liquid state behaviour.

LiV_2O_4 has a network with corner-shared tetrahedra of V ions. Recent inelastic neutron scattering experiments show that antiferromagnetic (AFM) correlation between V spins

develops and dominates the spin fluctuation below 30 K [4], while the spin dynamics strikingly changes from AFM to ferromagnetic (FM) spin fluctuations with increasing temperature [5]. Thus the spin system seems to suffer from geometric frustration at low temperature. In fact, on substituting small amounts of Zn [6] or Mn [7] for Li, the spin glass phase readily appears, suggesting that the substituted system is a frustrated magnetic metal. However, there is an open question about the relation between the HF ground state and spin frustration.

Very recently, a metal–insulator transition has been observed in a resistivity experiment under pressure [8]. This transition seems to be attributable to charge ordering of V ions as observed in isostructural AlV_2O_4; it has been reported that the configuration of charge ordering consists of three $V^{2.5-\delta}$ ions and one $V^{2.5+\delta}$ ion coupled with rhombohedral distortion along the (111) axis [9]. Takeda carried out a powder XRD measurement of LiV_2O_4 where the pressure dependence at the low temperature of 10 K was investigated. A structural transition from $Fd3m$ to $R3m$ which is similar to the charge ordering in AlV_2O_4 was observed [10]. Therefore, in order to understand the ground state of LiV_2O_4, it is important to clarify the character of low lying spin excitation under high pressure. We reported in a previous high pressure NMR study that antiferromagnetic fluctuations are enhanced with pressure application and show an opposite pressure dependence to that in usual Ce 4f HF systems [11]. However, the sample quality was not optimum and the NMR experiment was performed only down to 1.3 K. In the present work, we have developed a high pressure NMR technique that can be used up to 5 GPa and measured ^{7}Li NMR to elucidate the spin dynamics around the metal–insulator transition down to 60 mK, using a sample of the best quality.

2. Experimental details

Polycrystalline samples of LiV_2O_4 were prepared by solid state reaction at 700–750 °C in an evacuated silica tube for 48–72 h [7]. The samples were crushed into powder for measurements of the ^{7}Li NMR. Hydrostatic pressure was applied by an 'indenter cell' [12]. Since the sample space is very narrow (1.6 mm in diameter and 1.8 mm in height), the NMR coil is also tiny: the typical size is 1 mm diameter and 0.3 mm height. Experimental details will be published elsewhere. The pressure-transmitting medium was a Daphne oil (7373) and the generated pressure on the sample was determined from the pressure dependence of the superconducting transition temperature T_C for metallic lead. Fine grains of lead are inserted into the NMR coil with the sample powders. T_C for lead is measured by an AC susceptibility apparatus with a flowing AC current in the outer coil of the Cu–Be container. The diamagnetic change of the AC susceptibility was very sharp around T_C; the pressure distribution was estimated as ± 0.065 GPa at most, assuming the widening around T_C to be ascribable to the pressure distribution. Accordingly, the generated pressure is nearly hydrostatic.

3. Results and discussion

The ^{7}Li NMR spectra for LiV_2O_4 were measured at the frequency of 17.3000 MHz up to 4.74 GPa. Since the sample space of our cell is very small, the intensity of the signal is very low and the signal to noise ratio is 4 at 4.2 K. However, we confirmed in a previous paper that the pressure cell's effect (e.g. from the magnetism of the Ni–Cr–Al alloy and pressure distribution in the NMR coil) on the NMR measurement is negligible. Thus precise measurements of the Knight shift K could be performed within a maximum error of $\pm 0.03\%$. The observed NMR line is a sharp and symmetric one, indicating that the sample has good quality as pointed out in [3].

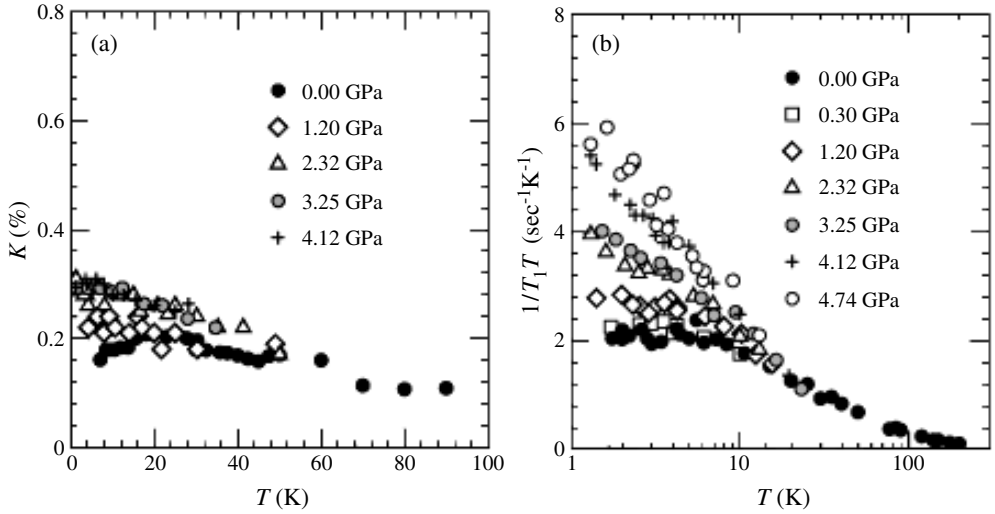

Figure 1. (a) and (b) show the pressure dependence of the Knight shift and $1/T_1T$ at the frequency of 17.3000 MHz, respectively.

Figure 1(a) shows the temperature dependence of K under high pressure. At ambient pressure, K has a broad maximum around 30 K corresponding to a T dependence of the uniform susceptibility. Although K is proportional to the magnetic susceptibility above 20 K, it is not proportional below 20 K, because a paramagnetic impurity term is added in the observed susceptibility at low temperature. Accordingly, K reveals the intrinsic pressure and temperature dependence of the uniform component of the spin fluctuations. Applying pressure up to about 2 GPa, K slightly increases at low temperature. However, K is pressure independent above the pressure of 2 GPa. This result suggests that the uniform susceptibility $\chi(\mathbf{q} = 0)$ also does not change under high pressure.

The nuclear spin–lattice relaxation time T_1 of ^{7}Li for LiV_2O_4 was measured up to 4.74 GPa and down to 1.3 K. Figure 1(b) shows the temperature dependence of $1/T_1T$ under high pressure. At ambient pressure, the relaxation rate shows heavy fermion behaviour with Korringa relation below 8.0 K and is identical to the previous results reported by other groups [1, 3]. On the other hand, $1/T_1T$ becomes larger on applying higher pressure below 20 K, which is a characteristic temperature (T^*) of the HF state in LiV_2O_4. Above 2.3 GPa, $1/T_1T$ does not obey the Korringa relation (the relation $T_1T =$ constant) down to 1.3 K. Since $1/T_1T$ is generally expressed as a $\mathbf{q}$ summation of the dynamical susceptibility $\chi(\mathbf{q})$, some AFM spin correlations with $\mathbf{q} \neq 0$ largely develop with applying pressure, taking account of the result that the uniform susceptibility is almost pressure independent. It is noted that the pressure dependence of T_1 for LiV_2O_4 is opposite to that for typical Ce HF compounds, such as $CeCu_{5.9}Au_{0.1}$ [13] and $CeCu_2Si_2$ [14].

In order to elucidate the intrinsic spin dynamics close to the insulating phase boundary, we measured the relaxation rate under the highest pressure of 4.74 GPa down to 60 mK. As seen in figure 2, it is clearly confirmed that $1/T_1T$ continues to increase down to 60 mK and that AFM spin fluctuations strongly dominate the low lying spin excitation in LiV_2O_4 below $T^* = 20$ K. However, no anomalies due to phase transitions to the magnetic ordering or superconducting states are observed down to 60 mK. Here the Knight shift is almost T independent between 0.06 and 1 K. Our NMR results indicate that the development of AFM spin fluctuations is essential for forming the HF ground state.

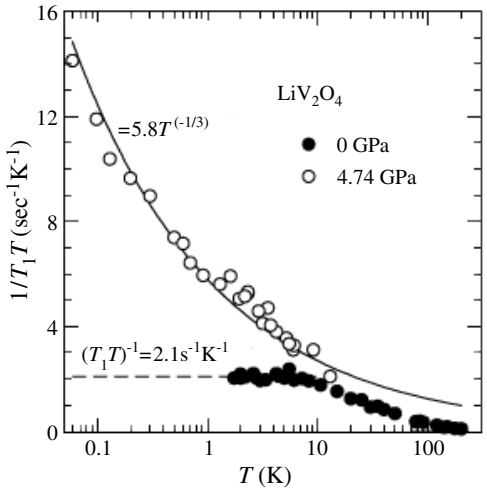

Figure 2. The temperature dependence of $1/T_1T$ under pressures of 0.00 and 4.74 GPa. The solid curve indicates a fitting to $CT^{-1/3}$.

Since AFM spin fluctuation is predominant below $T^* = 20$ K, it is of interest to compare the relaxation behaviour with a spin fluctuation theory, such as self-consistent renormalization (SCR) theory. In SCR theory, the relaxation rate is directly related to the staggered susceptibility χ_Q around the three-dimensional AFM instability, $1/T_1T \propto \sqrt{\chi_Q} \propto T^{-1/2}$ [17]. On the other hand, as seen in figure 2, $1/T_1T$ at 4.74 GPa satisfies the power law for temperature, $\prec T^{-1/3}$, between 0.06 and 10 K. Here the power is estimated by the least squares method and the solid curve indicates the fitting. Since this power law T dependence holds over a wide T range (over two orders of magnitude), it seems to be an intrinsic feature of spin fluctuations under high pressure. The deviation of the power between experiment and SCR theory suggests that the dynamical susceptibility of LiV_2O_4 has a broad maximum around the AFM wavevector **Q** and should be approximated by using a higher order term in the theoretical calculation. In order to reinforce these speculations, we need to measure the detailed pressure and temperature dependence of the relaxation rate and Knight shift fully, above 5 GPa. Furthermore, the itinerant picture should break down above the metal–insulator transition pressure of 6 GPa, so the relaxation behaviour must dramatically change in the insulating phase. It is of interest to elucidate the spin and charge dynamics around the phase boundary.

4. Conclusion

In conclusion, we reveal that AF spin fluctuations have an important role in forming the heavy fermion state in LiV_2O_4, and that the temperature dependence of the spin–lattice relaxation rate close to the pressure induced metal–insulator transition is different from that expected in the usual 3D spin fluctuation theory. It is noteworthy that the pressure dependence of $1/T_1T$ is opposite to that of typical Ce f-electron systems. Such dependence is quite puzzling and cannot be interpreted in terms of a pressure dependence of resistivity measurements, which may be a good test for checking the validity of theoretical attempts. In order to elucidate the change of the electronic structure under high pressure, a detailed analysis of the atomic position and inter-atomic bonding has been performed by a co-worker using XRD data obtained at BL10XU in SPring 8 [17].

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References

[1] Kondo S, Jonston D C, Swenson C A, Borsa F, Mahajan A V, Miller L L, Gu T, Goldman A I, Maple M B, Gajewski D A, Freeman E J, Dilley N R, Dickey R P, Merrin J, Kojima K, Luke G M, Uemura Y J, Chmaissem O and Jorgensen J D 1997 *Phys. Rev. Lett.* **78** 3729
[2] Urano C, Nohara M, Kondo S, Sakai F, Takagi H, Shiraki T and Okubo T 2000 *Phys. Rev. Lett.* **85** 1052
[3] Mahajan A V, Sala R, Lee E, Borsa F, Kondo S and Jonston D C 1998 *Phys. Rev.* B **57** 8890
[4] Lee S-H, Qiu Y, Broholm C, Ueda Y and Rush J J 2001 *Phys. Rev. Lett.* **86** 5554
[5] Krimmel A, Loidl A, Klemm M, Horn S and Schober H 1999 *Phys. Rev. Lett.* **82** 2919
[6] Ueda K, Fujiwara N and Yasuoka H 1997 *J. Phys. Soc. Japan* **66** 778
[7] Miyoshi K, Ihara M, Fujiwara K and Takeuchi J 2000 *Physica* B **281/282** 30
[8] Ueda H, Urano C, Nohara M, Takagi H, Kitazawa K, Takesita N and Mori N, unpublished
[9] Matsuno K, Katsufuji T, Mori S, Morimoto Y, Machida A, Nishibori E, Takata M, Sakata M, Yamamoto N and Takagi H 2001 *J. Phys. Soc. Japan* **70** 1456
[10] Takeda K, Kobayashi T C, Nishibori E, Takata M, Sakata M, Fujiwara K, Miyoshi K and Takeuchi J 2004 at press
[11] Fujiwara K, Yoshioka H, Miyoshi K, Takeuchi J, Kobayashi T C and Amaya K 2001 *Physica* B **312/313** 913
[12] Eremets M I, Amaya K, Shimizu K and Kobayashi T C 2001 *Rev. High Pressure Sci. Technol.* **7** 469
[13] Fujiwara K, Yoshioka H, Miyoshi K, Takeuchi J, Kohori Y and Kohara T 2000 *Physica* B **281/282** 361
[14] Kawasaki Y, Ishida K, Mito T, Thessieu C, Zheng G-Q, Kitaoka Y, Geibel C and Steglich F 2002 *Phys. Rev.* B **63** 140501(R)
[15] Fujimoto S 2002 *Phys. Rev.* B **65** 155108
[16] Lee J D 2002 *Preprint* cond-mat/0211261
[17] Ueda K and Moriya T 1975 *J. Phys. Soc. Japan* **38** 32