Critical Behavior of Susceptibility at the Nuclear Ordering Transition in $PrCu_6$

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The nuclear susceptibility and magnetization of a Van Vleck paramagnet $PrCu_6$ have been measured through the nuclear ordering transition. At zero magnetic field, the susceptibility shows a critical behavior at the transition temperature of 2 mK. This critical behavior shrinks and disappears as the applied magnetic field is increased. It is found that this behavior of the susceptibility is consistent with the electrical resistivity anomaly near the transition in its frequency and magnetic field dependence. The magnetization in magnetic fields shows a ferromagnetic increase at the transition, which coincides with the resistivity decrease in the ordered state. [S0031-9007(98)08321-5]

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Nuclear magnetic moments are about 1/1000 the magnitude of the electronic moments so the electronic magnitude of the interaction between nuclear spins is roughly 6 orders less than that of electron spins. Hence the expected nuclear magnetic ordering temperatures for pure metals are low, ranging from μK to pK, and demagnetization of nuclear spins themselves is necessary to reach their nuclear ordering temperatures. In these cases, the nuclear spin system is not in equilibrium with the electron spin system which remains at a higher temperature. In the past two decades, nuclear magnetic ordering for pure metals has been studied progressively based on the concept of spin temperature [1], and some new spin structures, quite different from those of the electron spin systems, were found [2].

There is another candidate for the nuclear magnetism of metals, the Van Vleck paramagnets, whose electronic ground state is a singlet in a crystal field. In Van Vleck paramagnets, nuclear spins couple strongly with electron spins through the hyperfine interaction [3] and order in the mK region due to an enhanced nuclear magnetic moment. Van Vleck paramagnets are, therefore, good candidates with which investigations of the nuclear magnetic ordering in thermal equilibrium to electron spin system can be carried out. Additionally the ordered state far below the transition temperature can be studied using a simple one stage copper nuclear demagnetization apparatus. The typical Van Vleck paramagnets are Pr compounds. We can study both nuclear ferromagnets and antiferromagnets in these Pr compounds by changing atomic species bound to Pr atoms and the anisotropy effect by selecting crystal structures. Moreover, we can investigate the nuclear ordering transition not only by measuring physical properties of nuclear spins (such as $PrNi_5$, $PrCu_6$, $PrIn_3$, $PrBe_{13}$) [4–9] but also by examining electronic properties [10–12].

In this Letter we have measured frequency-dependent nuclear susceptibility and static magnetization as a function of temperature and magnetic field through the nuclear ordering temperature and made a comparison with our former electrical resistivity measurement, where resistivity shows an anomalous behavior near the transition and decreases in the ordered state [11].

We prepared a single crystal of $PrCu_6$ grown by the Czochralski pulling method with a tungsten crucible in a helium atmosphere [13] and cut into a rectangular shape of $1.2 \times 2.8 \times 24$ mm, which corresponds to the $a \times b \times c$ axis directions, respectively. The sample $PrCu_6$ crystallizes in the orthorhombic $CeCu_6$ type at room temperature and changes to the monoclinic structure at low temperature [13]. In this crystalline field, nine folded degenerate states of a Pr^{+2} ion are split into nine singlet states. The residual resistivity ratio of this sample was 63, comparable to that of our former electrical resistivity measurement. Our sample contains less than 50 ppm of magnetic impurities, and we could not observe any obvious impurity effect in either the susceptibility or the magnetization measurements below 100 mK. The c axis of the sample was aligned parallel to the applied magnetic field: the same field orientation as our previous resistivity measurement. Magnetic fields were supplied by a saddle magnet immersed in the liquid helium bath and trapped in a niobium superconducting cylinder by heating it up to its superconducting transition temperature. The trapped fields were calibrated by a Hall sensor [14] located in the cylinder.

Contact between the sample and the thermal link connected to the copper nuclear demagnetization stage was established by press contact with screws. We used an rf-SQUID magnetometer in the conventional way with a bridge for susceptibility and magnetization measurements. Using a heater wound on the soft-solder line shield for the flux transformer, we can heat the superconducting flux transformer lead up to the normal state without any interference with the measurement even at the lowest temperatures. Since the current sometimes exceeds the

dynamic range of our SQUID magnetometer when the magnetic field was trapped or the magnetization grew so large, this heater plays an important role of reducing the current running through the superconducting flux transformer lead.

A ^{3}He melting curve thermometer was located at the same thermal link. We used the Greywall scale [15] above the antiferromagnetic ordering temperature of solid ^{3}He and Osheroff's data [16] below that temperature. During cooling steps, we measured both susceptibility and magnetization. In the magnetization measurement, we have to subtract the background which is altered by the changes in the demagnetization field of the copper nuclear stage. We can estimate experimentally the amount of magnetic flux by doing the demagnetization at higher temperatures, where the temperature dependence of the magnetization is small. We can also clearly distinguish between the magnetization and the effect of the demagnetization by the behavior of the SQUID output. The relaxation time of the magnetization after demagnetization was much longer, several hours at 5 mK and a few days below the ordering temperature, than the field sweep rate of the demagnetization. The measured values of the magnetization have been checked by warming with a heater, not by sweeping the demagnetization field. In spite of several flux jumps and drift that appeared sometimes while liquid helium was added to the cryostat, the reproducibility in our magnetization measurement was within $\pm 2\%$ for different runs.

We have measured susceptibility, $\chi = \chi' - i\chi''$, at different frequencies in various magnetic fields. Below 100 mK, both real and imaginary parts of the susceptibility show sharp peaks at the nuclear ordering temperature of about 2 mK. Figure 1(a) shows the temperature dependence of the real component of the nuclear susceptibility χ' at zero magnetic field. Here, we have subtracted the contribution of both Van Vleck and Pauli paramagnetic contributions and the signal caused by the mismatch of the astatic pair coils by using a temperature-independent value above 40 mK as a background. The subtracted values, depending on the frequency, are about 20% of the maximum values at the transition. The peak height of the susceptibility at the transition decreases with increasing frequency from 100 to 1000 rad/s, as expected in the region of $\omega\tau \sim 1$, from the following equation:

$$\chi' = \chi_0/(1 + \omega^2\tau^2), \qquad \chi'' = \chi_0\omega\tau/(1 + \omega^2\tau^2), \tag{1}$$

where we used the Debye assumption for the Casimir-du Pré equations [17]. Here, χ_0, τ, and ω are the static susceptibility, the spin-relaxation time, and the angular frequency of the alternating current passing through the primary coil, respectively. In Fig. 1(b), we show the inverse of the temperature-dependent susceptibility at 100 rad/s. Above 5 mK, the susceptibility shows Curie-Weiss behavior, and the obtained Weiss temperature is quite close to zero. Below 5 mK, the susceptibility increases ferromagnetically above the Curie-Weiss curve. The susceptibility decreases rapidly below the transition temperature as usually seen in the ferromagnetic state, where the internal field becomes large.

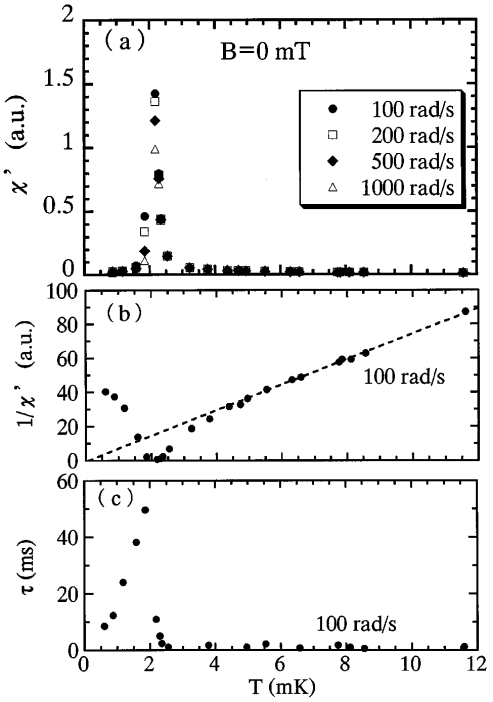

FIG. 1. (a) Susceptibility at various frequencies as a function of temperature obtained at zero magnetic field below 12 mK. The nuclear magnetic ordering occurs at 2.18 mK. (b) The inverse of the temperature-dependent susceptibility at the frequency of 100 rad/s. The line shows Curie-Weiss behavior. (c) Spin-relaxation time calculated from Eqs. (1) vs temperature.

To compare this result with our former impedance measurement at different frequencies, we use the following equations of the impedance Z:

$$Z = (l/S)\rho + i\omega(L + M),$$
$$= (1/S)\rho + L_0\varepsilon\omega(\chi'' + i\chi') + i\omega(L_0 + M), \tag{2}$$

where ω, ρ, l, and S are an angular frequency of the measurement, the resistivity, the length between the voltage terminals, and the cross-sectional area of the sample, respectively [10,18]. The first term represents the dc component of the resistance and the third term is frequency dependent but temperature independent, where M is the mutual inductance between the voltage and current leads. This frequency-dependent term has been subtracted in our analysis as a background using a higher temperature value. The second term shows the frequency-dependent loss component and the response component due to the susceptibility. Here we used the relation for the self-inductance, $L = L_0(1 + \varepsilon\chi)$, where L_0 is the empty

inductance, and ε is a geometrical factor of the sample. Note that this term has both frequency and temperature dependence and should be compared with the result of the susceptibility measurements. We show $\omega\chi''$ as a function of temperature and the result of resistivity in Fig. 2 and the inset. These sharp peaks of susceptibility near the transition correspond to the resistance anomaly at the transition [11]. The peak height increases with increasing frequency, but the frequency dependence of the susceptibility is a bit stronger than that of the resistance.

To investigate the critical behavior near the transition, we first have to determine the transition temperature T_c. In the susceptibility and magnetization measurements, it is difficult to fix the transition temperature, because the real component of the susceptibility reaches its maximum value at lower temperature than does the imaginary component with no sharp change in the magnetization. We therefore estimate the transition temperature using the thermal relaxation time of the magnetization. The relaxation time τ is given by the relation $\tau' = RC$, where C represents the sample heat capacity, and R is the boundary resistance between the thermal link and the sample. Assuming temperature-proportional boundary resistance at low temperatures, the longest thermal relaxation time corresponds to the heat capacity maximum, that is, the transition. The obtained transition temperature is 2.18 mK at zero magnetic field, and it coincides with the rapid growth point of the magnetization and the maximum point of the real component of the susceptibility. It is found that the spin-relaxation time obtained from the susceptibility data by using the relation $\tau = \chi''/\chi'\omega$, which is derived from Eqs. (1), becomes long near the transition (critical slowing down) as seen in Fig. 1(c).

To compare this susceptibility result with the resistivity result in magnetic fields, we have measured the imaginary part of the susceptibility by changing the applied magnetic field. The result obtained is shown in Fig. 3. The peak height at the transition decreases with increasing field and disappears above 4 mT. This result is also consistent with the field dependence of the resistance (inset of Fig. 3) near the transition. The peak height at the transition, which might depend on the sweep rate passing through the transition, shows much stronger field dependence than that of the resistance. Subtracting the resistivity anomaly (the peaks) near the transition, the dc component of the resistance [the first term in Eqs. (2)], which decreases in the ordered state, is obtained. We can attribute this resistivity decrease to ferromagnetic spin alignment as discussed below.

The magnetization as a function of temperature at several external magnetic fields is shown in Fig. 4(a). The magnetization increases a bit at the transition at 0 mT. When we increase the applied magnetic field up to 2 mT, the magnetization increases rapidly at the transition and saturates at a certain value as the temperature is lowered. This saturation value stays constant up to 20 mT. The saturation magnetization increases again, when we increase the magnetic field to 40 mT. This result

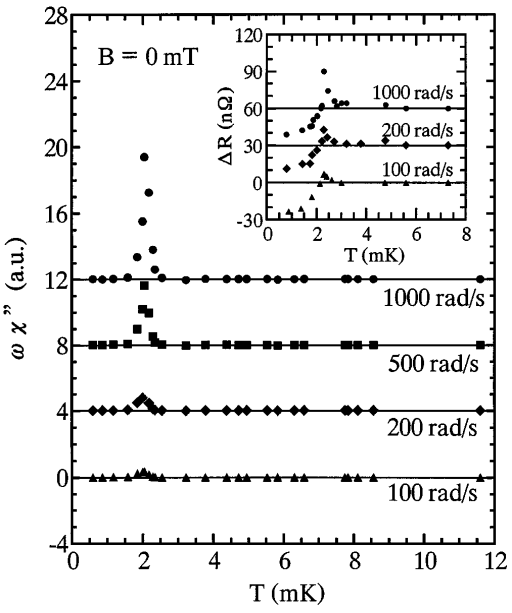

FIG. 2. Frequency dependence of the temperature-dependent $\omega\chi''$ at 0 mT. The zeros for the three upper data have been shifted upwards by 12, 8, and 4 units, respectively. These behaviors are quite similar to that of the resistance (see inset) [11].

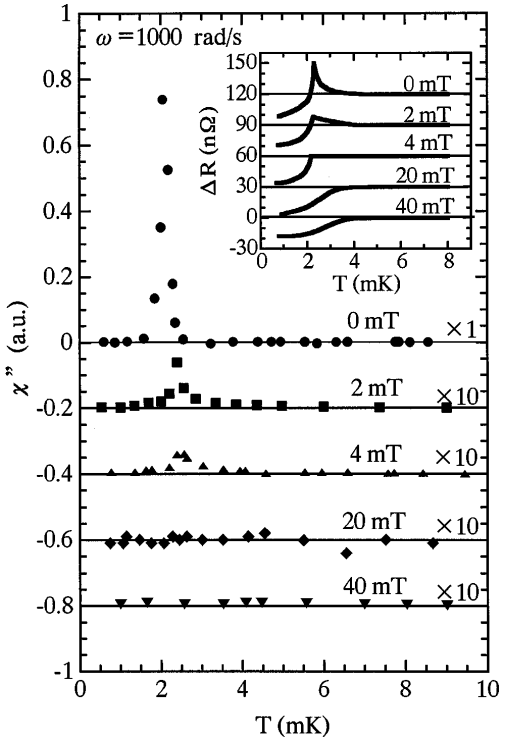

FIG. 3. Magnetic field dependence of χ'' at 1000 rad/s. The zeros for the four lower data have been shifted downwards by -0.2, -0.4, -0.6, and -0.8 units, respectively. This result is comparable to the field dependence of the resistance (the inset) [11].

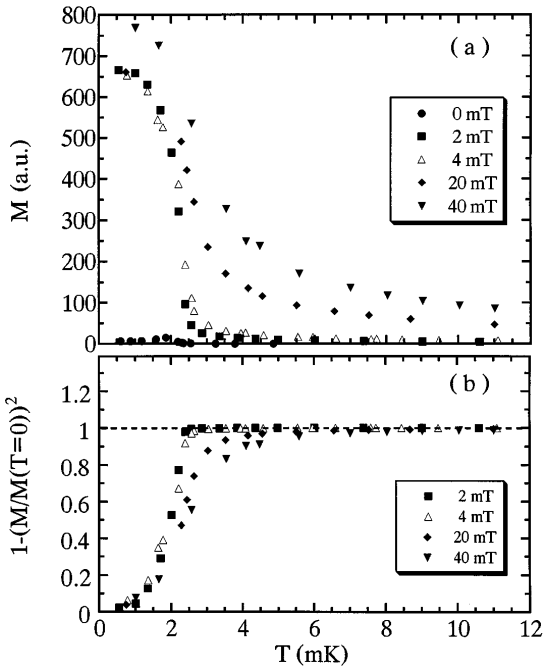

FIG. 4. Field dependence of the magnetization as a function of temperature. At 0 mT, a small increase of the magnetization can be seen. This result suggests the possibility of the ferromagnetic domain structure (see text). Rapid increase of the magnetization at the transition was observed at 2 and 4 mT, which suggests the ferromagnetic ordering. The rounding effect by the applied magnetic field is seen at 20 and 40 mT. (b) Points are the data of $1 - [M/M(T = 0)]^2$, which are comparable with the resistivity (see inset of Fig. 3).

is consistent with that obtained above 2 mK by Babcock *et al.* [7] and suggests ferromagnetic spin alignment.

Next we compare the magnetization with the resistivity ρ measured in the previous work [11]. When the scattering of conduction electrons is due to the localized moments S_i located at site i, ρ is expressed by the correlation function $\langle \delta S_i(t) \delta S_j \rangle$, where $\delta S_i = S_i - \langle S_i \rangle$. In enhanced nuclear magnets, S_i is replaced by the nuclear spin I_i [12,19]. Near the critical temperature, the correlation length diverges and the time dependence shows critical slowing down so that in ferromagnetic transition $\langle \delta I_i(t) \delta I_j \rangle$ turns proportional to $\langle I^2 \rangle - \langle I \rangle^2$, where I is the sum of I_i over sites i. Namely, ρ is proportional to $\langle M^2 \rangle - \langle M \rangle^2$ [20]. Substituting $\langle M^2 \rangle$ with $M(T = 0)^2$, we plot $1 - [M/M(0)]^2$ against T in Fig. 4(b). Comparing this figure with the inset of Fig. 3 we find that the relation $\rho \propto 1 - [M/M(0)]^2$ roughly holds.

We have observed magnetic hysteresis phenomena in the magnetization process in the ordered state, which supports the existence of a ferromagnetic domain structure at 0 mT. This magnetic domain structure can also explain why the electrical resistivity decreases even at 0 mT. The detail of the magnetization process in the ordered state along both the easy (b) and the hard (c) axes as a function of the magnetic field will be published elsewhere.

In summary, we have measured the susceptibility and magnetization of $PrCu_6$ through the nuclear ordering transition. The observed behavior of the susceptibility and the magnetization near the transition temperature agrees with that of the electrical resistivity in its frequency and field dependence.

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