cle simulation.[11]

Much of the work reported here was done during the period when one of the authors (R.N.S.) enjoyed the hospitality of the Institute for Advanced Study, Princeton, N. J., and of the U. S. Naval Research Laboratory, Washington, D. C.

*Work supported by the U. S. Energy Research and Development Administration and the U. S. Naval Research Laboratory.

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Strong Coupling between Liquid ^{3}He and Electron Spins at the Magnetic Phase Transition

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(Received 3 November 1975)

A steep dip in the nuclear-spin-lattice relaxation time, T_1, of liquid ^{3}He in contact with CuTA [copper tetrammine sulfate monohydrate, $Cu(NH_3)_4SO_4 \cdot H_2O$] has been observed near the ordering temperature, $T_N = 0.43$ K, of CuTA. Data show that the electron-spin fluctuation in CuTA plays an important role for the relaxation mechanism of liquid ^{3}He through the boundary interaction. An effective way of liquid-^{3}He cooling through this type of interaction is suggested.

Since the observation of the anomalous thermal boundary resistance between liquid ^{3}He and cerium magnesium nitrate (CMN) in the ultralow-temperature region by Abel *et al.*[1] in 1966, many theoretical[2-4] and experimental[5,6] investigations have been carried out to explain the origin of the phenomenon. Leggett and Vuorio[2] carried out an explicit calculation of this phenomenon in terms of the magnetic interaction between electron spins in CMN and ^{3}He nuclear spins. Guyer[3] rederived the boundary resistance for the same system using the relationship between the boundary resistance and the longitudinal relaxation time of interacting spin systems, and he pointed out that the strength of the coupling between electron spins and ^{3}He nuclear spins depends on the degree of synchronism between the motion of the two spins. Mills and Beal-Monod[4] re-examined theoretically the rate of energy transfer produced by the interaction between ^{3}He nuclear spins and electron spins. They suggest that the study of the longitudinal relaxation time, T_1, of the ^{3}He nuclei in contact with the magnetic salt, which has the magnetic phase transition in the low-temperature region, would be fruitful for the investigation of this boundary resistance problem. The present experimental work has been motivated by this suggestion.

I have chosen several magnetic salts as electron-spin systems to interact with the ^{3}He nuclear spin, and made ^{3}He NMR and T_1 measurements by the cw method. The results observed

for copper tetrammine sulfate monohydrate, $Cu(NH_3)_4SO_4 \cdot H_2O$ (hereafter abbreviated to CuTA), as an electron-spin system are remarkable and indicate that the electron spin plays an important role through the boundary interaction, and that the relaxation mechanism of liquid ^{3}He is strongly affected by the electron-spin fluctuation near the magnetic phase transition rather than in the well-ordered or the ordinary paramagnetic temperature region.

CuTA is a well-known magnetically one-dimensional substance, which has a three-dimensional antiferromagnetic ordering below $T_N = 0.43$ K. The magnetic and thermal investigations of this substance have been reported by many authors.[7,8] In the present work, the CuTA crystal plate, as a magnetic wall, is immersed in liquid ^{3}He. Three pieces of single-crystal CuTA are glued with Apiezon-N grease to the inside wall of a sample cell made of Pyrex glass. The total surface area of the three crystals is about 2.4 cm^2 and the volume of the sample liquid ^{3}He is 1.2 ml. The rf coil for the NMR measurement is placed around the cell without thermal contact with the cell. The cell is thermally anchored with a Kovar seal to the mixing chamber of a dilution refrigerator. The first derivative of the ^{3}He NMR absorption signal is recorded on a chart recorder. Although the oscillating level of the marginal detector was kept as low as possible within the limits of the detection sensitivity, slight saturation has been observed on the recorded first derivatives. The apparent NMR intensity proportional to the amplitude of the first derivative at applied magnetic field, $H_0 = 1.85$ kG, is plotted as a function of temperature in the upper half of Fig. 1. A steep peak of the apparent intensity is observed in the critical temperature region of CuTA. The maximum height of the peak is about 3 to 4 times larger than the signal height at a temperature of 0.47 K. Although the increase of the apparent intensity at 0.43 K is too intense to be explained by the disappearance of the saturation through T_1 shortening, it is not clear from the present measurement whether nuclear susceptibility enhancement exists or not at this temperature. The temperature dependence of the apparent NMR intensity, with the exception of the critical temperature region, is similar to the nuclear susceptibility of liquid ^{3}He reported by Thomson, Meyer, and Adams.[9]

The longitudinal relaxation time, T_1, has been measured as a function of temperature by observing the change in the NMR signal amplitude of liquid ^{3}He with time. The amplitude of the signal at successive time intervals decays towards its equilibrium value. The T_1 is found from the decay slope of the signal $M(t)$ as a function of time expressed in the form $M(t) = M_0[1 - \exp(-t/T_1)]$, where M_0 is the equilibrium value of the signal amplitude. The observed T_1 as a function of temperature is shown in the lower half of Fig. 1. In this figure, the observed T_1 changes rather monotonically with temperature except near the ordering temperature of CuTA. The observed T_1, averaged over the measured temperature region except near the critical region, is about 53 sec as shown by the dotted line in the figure.

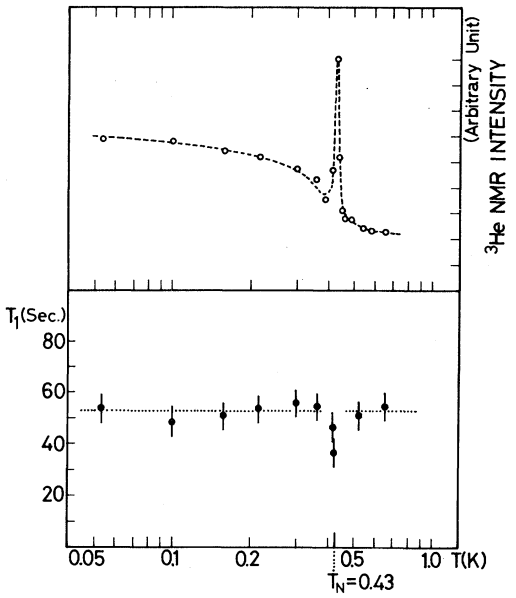

FIG. 1. Temperature dependence of apparent NMR intensity and nuclear-spin-lattice relaxation time, T_1, for liquid ^{3}He in contact with a wall made of CuTA crystals, which have antiferromagnetic ordering below $T_N = 0.43$ K.

Several investigators[10-12] have reported that T_1 of pure liquid ^{3}He is strongly affected by paramagnetic impurities on the wall. Low and Rorschach[10] have assumed that the observed net T_1 consists of a parallel combination of $(T_1)_{wall}$, resulting from paramagnetic impurity on the wall, and bulk relaxation $(T_1)_{bulk}$, and have derived an expression $(1/T_1)_{net} = (1/T_1)_{wall} + (1/T_1)_{bulk}$. According to their estimation, the intrinsic T_1 of pure liquid ^{3}He is about 400 sec at 2.0 K. In the present work, a net relaxation time similar to that in previous works is observed in the measurement between 0.2 and 1 K for the case where the cell contains neither CuTA crystals nor Apie-

zon-N grease. The observed average value of T_1, 53 sec, in Fig. 1 may be explained by the ordinary paramagnetic-impurity effect such as that treated by Low and Rorschach.[10] The further shortening in the critical temperature region results from the synchronous enhancement of the magnetic coupling between the motion of electron spins and of ^{3}He nuclear spins. This strong coupling is thought to be enhanced as a result of the critical slowing down of the frequency of the electron spin wave.

The strong coupling has also been observed in a preliminary boundary-resistance measurement. A relationship between T_1 and the boundary has been derived by Guyer.[3] The boundary resistivity R_B consists of a parallel combination of the magnetic dipolar resistivity R_M and phonon resistivity R_K.[13-15] Potentiometric measurements[6] on R_B between the liquid ^{3}He and the CuTA crystal have been done through the temperature region of the magnetic phase transitions of CuTA. The results obtained from several runs of the experiment show a steep decrease of R_B at the lower-temperature side within the region of the phase transitions of CuTA. The data will be published elsewhere.

In order to show that the NMR results in the strong coupling region are not caused by a spurious effect coming from the instrumentation but are indeed a real effect, two successively saturating trains of ^{3}He NMR absorption signals are given in Fig. 2. The recording traces in Figs. 2(a) and 2(b) have been obtained at a fixed detector frequency near 6 MHz, and by successive repetitions of the field sweeps which increase and decrease through the resonance field within a few gauss. Figure 2(a) is an example of the saturating signal trains at temperatures out of the phase-transition region of CuTA. During the recording, the temperature of the sample cell was kept nearly constant within the fluctuations caused by the field sweeping. A normal exponential decay towards the equilibrium amplitude is seen in this figure. Figure 2(b) is an example of the saturating signal trains at temperatures just near and at the entrance of the strong-coupling region. This is a really striking and impressive signal train. During the recording, the temperature of the sample cell slowly decreased starting from just above the temperature of the strong-coupling region. At the beginning of the recording, the temperature of the CuTA was out of the strong-coupling region. After four successive signals saturating like those in 2(a) at temperatures out of

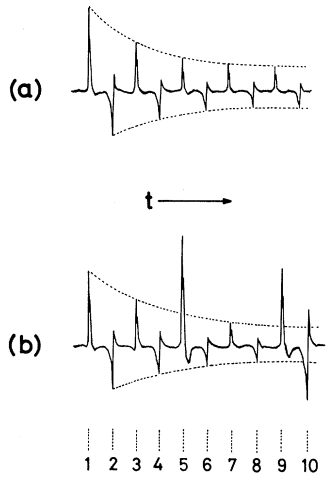

FIG. 2. Recorder traces of successively saturating ^{3}He NMR absorption signals. (a) An example of the signal trains at a constant temperature out of the phase-transition region of CuTA. (b) An example of the signal trains at temperatures just near and at the entrance of the strong-coupling region.

the strong-coupling region, an abrupt increase of the fifth amplitude occurred at a temperature just at the entrance of the strong-coupling region. On the occasion of the fifth signal, the temperature difference between CuTA and ^{3}He due to thermal boundary resistance had probably decreased by the strong coupling so that the temperature of CuTA has shifted out of the strong-coupling condition. Therefore the amplitude of the sixth, seventh, and eighth signals are those at temperatures out of the strong-coupling region. The strong-coupling condition again came back on the sweeps after the ninth signal. The duration between the first and the last signals in the 2(b) is about 200 sec, and the temperature difference between that at the first signal and that at the fifth signal is about 5 mK. Whereas it has been observed that in the measurement with temperature kept constant in the strong-coupling region, all of the amplitudes in the signal train have been strongly enhanced, when the strong-coupling occurs neither frequency shift of the ^{3}He resonance line nor distortion in the line shape have been observed. This is also evident in Fig. 2(b).

The boundary resistance between liquid helium and a solid is one of the most important practical problems in the few-millikelvin or submillikelvin region. When the liquid helium is ^{3}He and the solid is a paramagnetic substance, the magnetic coupling between ^{3}He nuclear spins and electron spins in the paramagnetic substance is of practi-

cal interest as a reducing mechanism for the boundary resistance as well as of fundamental interest for surface phenomena. In the references concerning the boundary resistance between liquid ^{3}He and CMN,[1,5,6,13] or between liquid ^{3}He and a metal containing magnetic impurity,[16] one sees the linearly temperature-dependent R_M effective in the very low-temperature region. However, the reduction in R_B through the contribution of R_M is still not large for practical use. It is worthwhile to emphasize here from the view point of the present investigation that the magnetic coupling is strongly enhanced under the condition of the synchronism between the motion of ^{3}He spins and of electron spins. As a natural consequence, it is suggested that by seeking the condition of synchronism in the critical-temperature region of CMN, a more effective reduction in R_B is probably obtained in the ^{3}He-CMN system. In the system, liquid ^{3}He may be cooled effectively during the demagnetization of CMN, for example, as the lowering field and CMN temperature are stopped at the point fulfilling the condition of the strong coupling. For ^{3}He cooling with metal, as a nuclear refrigerant, containing magnetic impurity, the same method might be expected too.

The author wishes to thank Professor Y. Nishina and Professor A. Ohtsubo for valuable discussions and encouragement and Takashi Sato for his assistance during the experiments.

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Theory of the Structural Phase Transformations in Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ)*

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An order parameter theory is derived and used to explain the observed structural phase transformations in tetrathiafulvalene tetracyanoquinodimethane. It is shown that there should be three transitions. One set of chains orders at 54 K, the other at 47 K. The modulation wave vector in the $\vec{a}^*$ direction is equal to $a^*/2$ between 54 and 47 K, increases as $a^*/2+\lambda(47-T)^{1/2}$ between 47 and 38 K, and locks to a value of $a^*/4$ below 38 K as a consequence of Umklapp terms in the free energy.

X-ray[1] and neutron[2] scattering studies of tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) have revealed structural phase transformations with a number of unusual features. In these experiments, it appeared that there were two transitions, one at 38 K, the other at 54 K. At low temperatures, there was a $4\vec{a}\times 3.4\vec{b}\times\vec{c}$ modulation relative to the undistorted lattice and, as the temperature was raised above 38 K, the modulation period in the $\vec{a}$ direction began to de-