Investigation of spin-lattice relaxation in antiferromagnets at ultralow temperatures

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An investigation was made of the spin-lattice relaxation and of the average magnetization of ^{55}Mn nuclei in $MnCO_3$ and $CsMnF_3$ at temperatures 1–0.05 K. It was found that the relaxation times increased as a result of cooling in accordance with a power law (characterized by an exponent ranging from -3 to -5) and they reached 10–100 h at 0.05 K.

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Investigations involving creation of a high degree of orientation of the spins of nuclei which are in thermal equilibrium with the lattice of a solid are pursued at present actively in various branches of physics. In these experiments the substances used are normally magnetically ordered and the orientation of the nuclear spins is the result of alignment of the spins along an internal hyperfine field $H_n \approx 10^5$–10^7 Oe at temperatures of the samples such that $kT \lesssim \mu_n H_n$ (this represents the energy of a nuclear spin in the hyperfine fields). One of the important problems is then the establishment of a thermal equilibrium between the nuclear spin system and the lattice of a sample. However, at temperatures $T < 1$ K the processes of establishment of such an equilibrium in magnetically ordered substances (nuclear spin-lattice relaxation) are little known and the reported experimental studies have been concerned mainly with the relaxation of impurity nuclei in a magnetic matrix.[1]

We shall report a study of the spin-lattice relaxation of the host ^{55}Mn nuclei in antiferromagnetic insulators $MnCO_3$ and $CsMnF_3$ characterized by a large dynamic frequency shift of NMR at temperatures $T < 1$ K. These substances were selected for the following reasons.

1) The dynamic frequency shift of NMR has been investigated quite thoroughly (see, for example, the review in Ref. 2). The magnitude of this shift is governed by the orientation[2)] of the spins of the ^{55}Mn nuclei. Consequently, the behavior of the nuclear magnetization can in this case be determined from the positions of the NMR spectra, which should improve greatly the precision of the measurements.

2) The magnetic spectra of these substances exhibit a gap with an energy ≈ 1 K due to the hyperfine interaction, so that measurements carried out in a wide temperature range make it possible to separate the magnon, magnon-phonon (important at temperatures $T > 1$ K), and phonon contributions to the relaxation process.

3) At $T \approx 0.1$ K both $MnCO_3$ and $CsMnF_3$ exhibit a considerable ($\sim 30\%$) deviation of the average magnetization of the ^{55}Mn nuclei from the value expected in the case of weakly interacting (with one another) nuclear spins in a hyperfine field.[3] This very interesting result can be confirmed by investigating the spin-lattice relaxation times with the aim of showing that the nuclear spin system is in thermal equilibrium with the lattice under experimental conditions.

SAMPLES AND MEASUREMENT METHOD

A crystal of $MnCO_3$ is a two-sublattice antiferromagnet exhibiting a weak ferromagnetism ($T_N = 32$ K), whereas $CsMnF_3$ is a six-sublattice antiferromagnet ($T_N = 64$ K). Both substances exhibit the easy-plane anisotropy. At liquid helium temperatures the vibrations of the nuclei are coupled strongly to oscillations of the electron spin system and this results in a dynamic NMR frequency shift which has been investigated by continuous NMR methods in the case of $CsMnF_3$ crystals[4,5] and $MnCO_3$ crystals,[6] as well as by pulsed NMR methods.[7,8] The NMR spectra of these substances are described by the formula

$$\nu_n^2 = \nu_{n0}^2 \frac{\nu_{e0}^2}{\nu_{e0}^2 + \nu_T^2}, \qquad \nu_T^2 = 2\gamma_e^2 H_E A \langle m \rangle, \tag{1}$$

where ν_{n0} and ν_{e0} are the unshifted NMR and antiferromagnetic resonance (AFMR) frequencies; γ_e is the atomic hydromagnetic ratio; H_E is the exchange field; A is the hyperfine interaction constant. In this range of temperatures the behavior of the nuclear magnetization is described by the Curie law, so that we have $\nu_T^2 \propto 1/T$. The values of the constants can be found in Refs. 4–8. The spin-lattice relaxation of the ^{55}Mn nuclei had been investigated by the method of saturation of an NMR line[4,6] and by the stimulated echo method.[7] The two methods gave comparable results. In the case of $CsMnF_3$ the spin–lattice relaxation time was found to depend strongly on temperature and magnetic field[5]:

$$T_1 \propto H^{-\alpha} T^{-\beta}, \text{ where } \alpha = 1-2,\ \beta = 4.5-5.$$

This behavior of T_1 is explained in Refs. 5 and 6 by the contribution of two- and three-magnon scattering processes to the relaxation under investigation. In the case of $MnCO_3$ the relaxation time T_1 depends weakly on temperature and magnetic field ($|\alpha|, |\beta| \lesssim 0.5$), which is related to the strong influence of impurities on the relaxation process.[8]

Our $MnCO_3$ single crystals were grown at the Institute of Crystallography of the USSR Academy of Sciences by N. Yu. Ikornikova, whereas $CsMnF_3$ crystals were grown at the Institute of Physics Problems of the USSR Academy of Sciences by S. P. Petrov.[3)] The quality of the samples deduced from the value of T_1 was close to those investigated in the studies reported in Refs. 5, 7, 8, but somewhat poorer than

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those used by Witt and Portis[4] (T_1 was an order of magnitude less).

An efficient solution cryostat constructed at the Institute of Physics Problems of the USSR Academy of Sciences was used to cool the samples: it maintained stably a given temperature for a time limited only by the patience of the experimenters. This cryostat could maintain temperatures down to 0.007 K, but it was found in the course of the above experiments that cooling of the nuclear subsystem to temperature below 0.05 K was practically impossible because of the extremely long spin-lattice relaxation times. Therefore, the investigations were limited to temperatures of 0.05 K. The temperature of helium in the solution chamber of the cryostat was measured with carbon resistance thermometers calibrated using a platinum NMR thermometer made by Instruments for Technology. The samples and thermometers were placed directly in the solution chamber of the cryostat. A static magnetic field was created by a superconducting solenoid. Radio-frequency (rf) radiation was introduced into the solution chamber along coaxial lines short-circuited by two-turn coils. A sample was placed at the center of a coil and oriented so that the static and alternating magnetic fields were mutually perpendicular and were acting in the basal plane of a sample. The NMR signal of the ^{55}Mn nuclei was recorded by direct observation of the spin echo or free precession after short rf pulses. The observation method and the spectrometer used were described in Ref. 7. Heating by the rf field was avoided when the repetition frequency of the probe pulses was sufficiently low (1–0.1 Hz) so that the average power absorbed by a sample was $P_{\text{av}} \approx 10^{-6}$–$10^{-9}$ W in the spin echo observations and $P_{\text{av}} \approx 10^{-10}$ W in the free precession case.

As shown in Ref. 6, a system exhibiting a dynamic frequency shift can readily be overheated to a given temperature T^* by applying a sufficiently powerful rf field of frequency $f = \nu(H, T^*)$. We used the same method in order to overheat the nuclear spin system. After overheating, the system cooled down to its equilibrium state in accordance with the exponential law

$$\frac{\nu^2(t)-\nu^2(H,T)}{\nu^2(H,T^*)-\nu^2(H,T)} = \exp\left(-\frac{t}{T_1}\right). \tag{2}$$

We could determine the value of T_1 by measuring the NMR frequency $\nu(t)$ as a function of time.

It was found in practice to be more convenient if the rf field frequency was kept constant. Therefore, the measurements were carried out as follows. Firstly, using a given value of f_{rf} of the rf frequency, the maximum of the free precession signal was used to find the resonance field H_T. Then, the magnetic field was reduced to H^* and an additional oscillator generating the same carrier frequency emitted one or several pulses of ~ 1 W power and ~ 1 msec duration. The value of H^* was selected so that the overheating $\Delta T/T$ was 5–10%. The occurrence of overheating was deduced from complete disappearance of the free precession signal near H_T and its appearance near H^*. Next, the sample was subjected to periodic probe rf pulses and the position of the free precession signal was used to determine the instantaneous values of the resonance field $H(t)$. The spin–lattice relaxation time was then estimated from

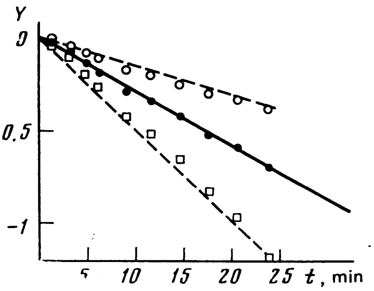

FIG. 1. Position of the NMR line of ^{55}Mn in CsMnF$_3$ after overheating, plotted as a function of time. $H_C = H_T = 9.2$ kOe (●), $H_C = H_T + 150$ kOe (○), $H_C = H_T - 75$ Oe (□), $T = 0.16$ K, $f = 549$ MHz.

$$\begin{gathered}\exp\left(\frac{-t}{T_1}\right) = \frac{H_T^2 - H^2(t)}{H_T^2 - H^{*2}},\\ \exp\left(\frac{-t}{T_1}\right) = \frac{H_T[H_T+H_D] - H(t)\,[H(t)+H_D]}{H_T[H_T+H_D] - H^*[H^*+H_D]}\end{gathered} \tag{3}$$

representing a conversion of Eq. (2) to suit the experimental conditions. The first expression in Eq. (3) applies to CsMnF$_3$ and the second to MnCO$_3$. Here, H_D is the Dzyaloshinskiĭ field. A typical graph used to determine the relaxation time is shown in Fig. 1.

POSITIONS FOR NMR SPECTRA OF ^{55}Mn

When the solution chamber was cooled rapidly, the observed influence of temperature on the NMR spectra was approximately the same as that reported in Ref. 3. However, after prolonged (of the order of tens of hours) storage of a sample at a constant temperature it was found that the NMR line of ^{55}Mn drifted and heating of the solution chamber manifested a hysteresis indicating that a thermal equilibrium was not yet attained. Therefore, the main attention was concentrated on the establishment of a thermal equilibrium between the spin system of the ^{55}Mn nuclei and the helium in the solution chamber of the cryostat. The nuclear subsystem could be off equilibrium first, because of the long spin-lattice relaxation times of the nuclei and, secondly, because of the Kapitza thermal jump between the investigated crystal and liquid helium; it could also be due to the heat supplied by the rf pulses. In the last case the overheating could be governed by the rf power, whereas in the first two cases it could determined by the cooling time. Our experiments showed that a change in the power and repetition frequency of the probe pulses within the intervals 0.1–5 Hz and 10^{-3}–10^{-2} W had no effect on the position of the NMR line and this excluded the possibility of overheating of the samples due to the absorption of the rf power. Estimates of the Kapitza heat resistance (carried out on the basis of Ref. 3) gave much shorter times for the establishment of an equilibrium than those found experimentally. Morever, our measurements showed that when the external magnetic field was removed, the rate of establishment of an equilibrium increased by an order of magnitude. Consequently, under the experimental conditions used in our case the establishment of a thermal equilibrium was determined by the process of spin-lattice relaxation of the ^{55}Mn nuclei.

A thermal equilibrium was established by keeping a sample for sufficiently long at some temperature of the solution bath in zero magnetic field. Then, a magnetic field was applied. In the range of relatively short relaxation times it was found that a prolonged storage in a magnetic field gave rise to the same equilibrium value of $\nu(H, T)$ as the storage of a sample in the absence of a field and its subsequent application. The spin-lattice relaxation time was measured in the presence of a magnetic field by a method described earlier. Figure 1 shows the time dependence of the quantity

$$Y=\ln\{[H_c^2-H^2(t)]/[H_c^2-H^2(0)]\}$$

for CsMnF$_3$. This dependence fits well the exponential curve. The accuracy of determination of the resonance field at the equilibrium temperature of the nuclei was checked by recalculating the experimental points assuming that the equilibrium field was $H_T + 150$ Oe (open circles) and $H_T - 75$ Oe (open squares). In both cased there was a deviation from the exponential curve indicating that the equilibrium field was determined to within ± 50 Oe. Moreover, the knowledge of the relaxation and cooling times enabled us to estimate the likely overheating. The experimental conditions were selected so that such overheating did not exceed $\Delta T/T \approx 0.05$.

Our NMR spectra of ^{55}Mn could be used together with Eq. (1) to calculate ν_T and, therefore, the temperature dependence of the average magnetization of the ^{55}Mn nuclei shown in Fig. 2a for MnCO$_3$ and in Fig. 2b for CsMnF$_3$. The continuous curves in these figures represent the Brillouin $B_{5/2}(\mu_n H_n/kT)$ describing the temperature dependence of the average magnetization in a hyperfine field H_n in the case of noninteracting nuclear moments μ_n (the values of the constants were taken from Refs. 4–7). Clearly, our results are described satisfactorily (within the limits of the experimental error) by this function. Consequently, the indirect interaction between the spin of the ^{55}Mn nuclei in the two crystals (known as the Suhl-Nakamura interaction) is far too weak to influence significantly the main thermodynamic properties of the nuclear spin system at temperatures $T \gtrsim 0.05$ K. The results of Ref. 3 can be explained by the fact that the total time of an experiment (several hours) was far too short to establish a thermal equilibrium between the spin system of the nuclei and the atomic lattices of the samples.

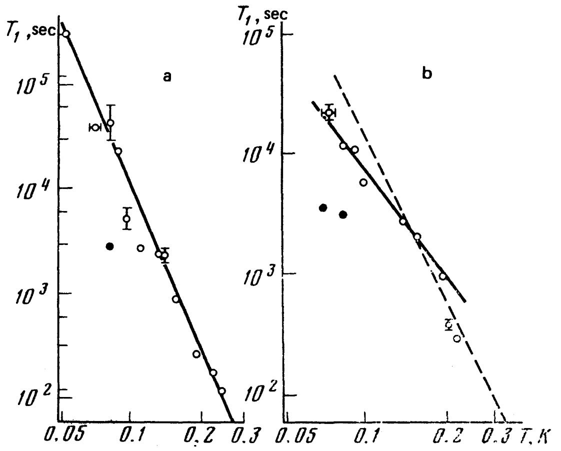

FIG. 3. Temperature dependences of the spin-lattice relaxation time of the ^{55}Mn nuclei in MnCO$_3$ (a) and CsMnF$_3$ (b) determined at the NMR frequency of 539 MHz.

SPIN-LATTICE RELAXATION OF ^{55}Mn NUCLEI

Our temperature dependence of the spin-lattice relaxation times are plotted in Fig. 3a for MnCO$_3$ and in Fig. 3b for CsMnF$_3$. Since in order to study relaxation in zero magnetic field (black dots in Fig. 3), we had to apply briefly a magnetic field in order to determine the NMR line position, the results obtained should be regarded as preliminary estimates and the attention should be concentrated on the process of relaxation in the resonance fields corresponding to the NMR frequency $\nu_n = 549$ MHz. In the case of MnCO$_3$ the dependence $T_1 \propto T^{-5.2 \pm 0.3}$ was obeyed quite accurately at all the investigated temperatures. Extrapolation of this dependence toward higher temperatures showed that the in the region of 1 K there should be an abrupt change in the relaxation mechanism. In the case of CsMnF$_3$ at temperatures $T < 0.02$ K the dependence was $T_1 \propto T^{-3}$; however, the points at the

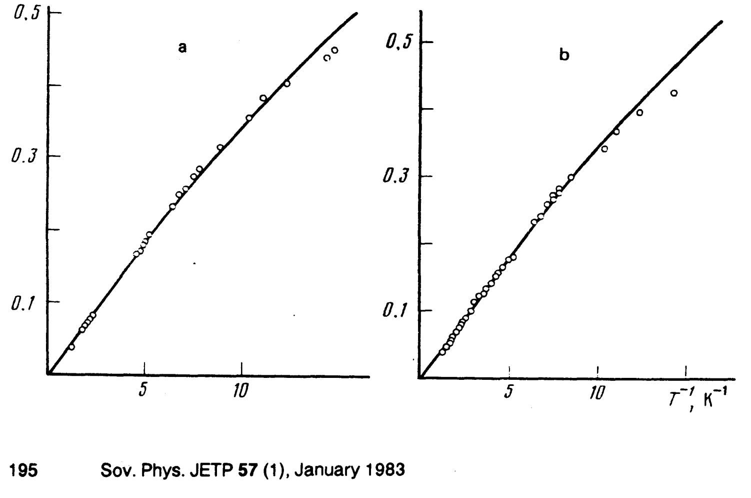

FIG. 2. Temperature dependences of the average magnetization of the ^{55}Mn nuclei in MnCO$_3$ (a) and CsMnF$_3$ (b) normalized to the magnetization at $T = 0$.

end of the range indicated a transition to a stronger temperature dependence which , when matched with our data obtained at $T = 1.7$ K, corresponded to $T_1 \propto T^{-4.5}$ (shown dashed in Fig. 3b), in agreement with the results of Welsh[5] obtained in the range 4.2–0.5 K. The measurements of Welsh were carried out in a static resonance field and the dependence $T_1 \propto T^{-5}$ was obtained. Conversion of this dependence to the conditions of our experiments carried out in the $\nu_n = \text{const}$ case reduced the power exponent so that $T_1 \propto T^{-4.5}$. Consequently, we could assume that the process of spin–lattice relaxation of the ^{55}Mn nuclei in $CsMnF_3$ was due to one mechanism throughout the investigated range 4.2–0.2 K. This was in conflict with the conclusion reached in Refs. 5 and 6 where the process of nuclear spin-lattice relaxation observed in the same substance at $T = 4.2$–1.5 K was attributed to magnon processes because these should give rise to an additional exponential rise of T_1 at temperatures $T \lesssim 1$ K.

The hyperfine gap in the spectrum of acoustic magnons of $MnCO_3$ and $CsMnF_3$ increases on cooling as $T^{-1/2}$ and at temperatures ~ 1 K becomes comparable with kT. Therefore, in the range $T < 1$ K the processes involving electron magnons are frozen out and the nuclear spin-lattice relaxation may be due to phonon scattering. Then, in the case of one-phonon processes we can expect, by analogy with paramagnetic relaxation, a linear temperature dependence (and in the case of two-phonon processes a stronger power dependence) of the nuclear spin-lattice relaxation rate.

The nuclear spin-lattice relaxation due to one-phonon processes in antiferromagnetic insulators was considered by Gladkov[10] for temperatures $T \approx h\nu_{n0}/k$. (In the case of $MnCO_3$ and $CsMnF_3$ we have $h\nu_{n0} \approx 0.003$ K.) Unfortunately, the temperature dependences of T_1 obtained by Gladkov cannot be extrapolated to higher temperatures because this gives a physically meaningless result of an increase in T_1 on increase in temperature. Extrapolation of our data to 0.03 K gives $T_1 \approx 6 \times 10^6$ sec for $MnCO_3$ and $T_1 \approx 3 \times 10^5$ sec for $CsMnF_3$. Estimates of the spin-lattice relaxation time for these substances carried out on the basis of Ref. 10 give $T_1 \approx 10^9$–10^{10} sec. However, this discrepancy is not too serious because the measured values of T_1 can vary by an order of magnitude from one sample to another (this applies at least at $T \approx 4$ K). The processes of nuclear spin-lattice relaxation involving two phonons in antiferromagnetic insulators were investigated theoretically only at helium temperatures.[9] However, by analogy with paramagnetic relaxation, these processes could be characterized by fairly high power exponents in the temperature dependence of T_1. (In the case of paramagnetic relaxation the dependences are $T_1 \propto T^{-(5-9)}$. We can therefore assume that in the investigated temperature range it is the two-phonon processes that are responsible for the spin-lattice relaxation of the ^{55}Mn nuclei in $MnCO_3$ and $CsMnF_3$ crystals.[4)]

A comparison of our results with those obtained at higher temperatures demonstrates an interesting feature. In fact, in the case of $MnCO_3$ in the range of existence of magnon relaxation processes the time constant T_1 is two orders of magnitude less than for $CsMnF_3$. This large difference is due to the influence of impurities,[5] because impurities reduce the magnitude of T_1 and lower the power exponent in its temperature dependence, as demonstrated by a comparison of the results reported in Refs. 5 and 7. On the other hand, at $T \approx 0.1$ K the rates of nuclear spin-lattice relaxation in these substances are of the same order of magnitude. Hence, we can assume that impurities that accelerate greatly the process of relaxation at $T > 1.5$ K have much less effect at higher temperatures. The reason for the reduction in T_1 in zero magnetic field cannot be identified without further studies. We may surmise that this reduction is due to a strong increase in the frequency range of nuclear spin waves so that additional groups of phonons are involved in the relaxation processes.

We would like to conclude by stressing an important feature. In the case of magnetically ordered insulators with relatively high values of the average nuclear magnetization (orientation) the nuclear spin-lattice relaxation time becomes fairly long (10^5–10^7 sec in our case), which must be allowed for very carefully in experiments on materials of this kind.

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[2)] We shall find it more convenient to use a similar concept of the average (over the magnetic sublattice) magnetization of the nuclear moments.

[3)] The authors are grateful to N. Yu, Ikornikov and S. V. Petrov for supplying the samples.

[4)] However, it should pointed out that the problem of validity of extrapolation of the results of Ref. 9 to $T < 1$ K has not yet been solved.

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[1] G. V. H. Wilson and D. H. Chaplin, Hyperfine Interact. **10**, 1981 (1981).

[2] Yu. M. Bun'kov and B. S. Dumesh, Problemy magnitnogo rezonansa (Magnetic Resonance Problems), Nauka, M. 1978.

[3] B. S. Dumesh, Pis'ma Zh. Eksp. Teor. Fiz. **24**, 167 (1976) [JETP Lett. **24**, 145 (1976)].

[4] G. L. Witt and A. M. Portis, Phys. Rev. **136**, A1316 (1964).

[5] L. B. Welsh, Phys. Rev. **156**, 370 (1967).

[6] V. A. Tulin, Zh. Eksp. Teor. Fiz. **55**, 831 (1968) [Sov. Phys. JETP **28**, 431 (1969).

[7] Yu. M. Bun'kov and B. S. Dumesh, Zh. Eksp. Teor. Fiz. **68**, 1161 (1975) [Sov. Phys. JETP **41**, 576 (1975)].

[8] Yu. M. Bun'kov and S. O. Gladkov, Zh. Eksp. Teor. Fiz. **73**, 2181 (1977) [Sov. Phys. JETP **46**, 1141 (1977)].

[9] V. S. Lutovinov and V. L. Safonov, Fiz. Tverd, Tela (Leningrad) **23**, 2759 (1981) [Sov. Phys. Solid State **23**, 1615 (1981)].

[10] S. O. Gladkov, Fiz. Tverd. Tela (Leningrad) **23**, 2686 (1981) [Sov. Phys. Solid State **23**, 1575 (1981)].

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