Nuclear Magnetic Relaxation in Sc Metal

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Abstract

The nuclear magnetic relaxation in scandium metal is investigated at liquid helium temperature for both single crystal and powder samples. The obtained temperature and field dependence of the Korringa constant are described by the means of the spin fluctuation theory. It is shown that one of the reason for the high field decreasing of the relaxation rate is the quenching of spin fluctuations. The other possible reason is the magnetic impurity influence. The reasons of the existing variations of the Korringa constant are discussed. The possible sources of non-single exponential relaxation are investigated.

I. INTRODUCTION

The interest for investigations of the behavior of nuclear spin system in scandium $^{45}$Sc ($I = 7/2$) metal comes from two sides at least. First of all, scandium is the first of transition metal and has only one $3d$ electron. But among transition metals possessing unique magnetic properties as a result of their $3d$ electrons scandium is probably the least understood, although in principle with only one $d$ electron it might be expected to be one of the best understood. The reason for such an absence of information is the impossibility before recent years [1] to get high purity scandium metal, especially with respect to the iron content.

Secondly, scandium is one of the metals where it could be possible to get and to investigate the nuclear magnetic ordering [2], [3]. Due to the smallness of the Korringa constant the nuclear spin-relaxation time is so short that the temperature of the conduction electrons and the temperature of nuclear spins are practically equal during experiment. It means that the exchange interaction between nuclear spins is rather strong that should lead to rather high temperatures of nuclear ordering (order of $\mu K$ while in such metals as Cu, Ag and Rh the corresponding temperatures have the order of few $nK$ and even of hundreds $pK$ [4]). Nuclear magnetic resonance (NMR) besides the knowledge of the parameters of nuclear spin
system yields information about conduction electron subsystem not immediately deducible from the band structures. In particular, the core electrons and the valence electrons give the distinct contributions to the Knight shift and nuclear magnetic relaxation time.

Accordingly to the above-mentioned it becomes to be clear the validity of the correct determination of the nuclear spin-lattice relaxation time from measurements of nuclear longitudinal magnetization evolution. Not so extensive NMR investigations in Sc metal [3]-[11] in the temperature range 0.001 ÷ 300K gave rather different values for the Korringa constant $K$ (from 0.09 sec·K to 1.6 sec·K) in the dependence on experimental conditions, particularly on the applied magnetic fields (see Table 1). It should be noted that in zero magnetic field (nuclear quadrupole resonance investigations [13]) the value of the Korringa constant obtained from the longest magnetization decay is extremely low, namely 0.09 sec·K. A priori it might be expected that such magnetic field dependence of the Korringa constant could be explained as the result of spin fluctuation influence. It is well known that the heat capacity at high magnetic fields is decreasing due to the spin fluctuation quenching [14]. As for nuclear magnetic relaxation such influence was observed for Sc intermetallic alloys [13]. But in the case of Sc pure metal there is no information about spin fluctuation influence on the nuclear spin system. It should be noted here that the recent theoretical calculations of spin relaxation times and susceptibilities on the basis of magnetic correlation functions [16] showed the importance of taking into account the properties of Fermi surface as well as the band structure in a finite energy range. Nevertheless in the framework of this approach it is impossible to explain the variation of the Korringa constant in the different experiments.

The present work reports about long time experimental and theoretical investigations of nuclear magnetic resonance in pure scandium metal (powders and single crystal). The special attention has been payed to the possible sources for non-exponential relaxation such as non-complete saturation of NMR line, the heating of conduction electron subsystem and influence of spin fluctuations.
II. SAMPLES.

The purity of our powder sample which we bought from Rare Metallic Co., Ltd. is 3N. A single crystal used in our experiments was grown in Ames Laboratory. It has a dimension of 3.5x2.0x27 mm$^3$ with the long direction parallel to the a-axis. The main magnetic impurities in our specimen analyzed in Ames Laboratory are 3 at. ppm Fe, 0.23 at. ppm Cr and 3.2 at. ppm Mn.

III. NMR SPECTRA.

Because of hexagonal symmetry NMR spectrum of $^{45}$Sc ($I = 7/2$) should consist of the main central peak with six satellites. The anisotropy of the Knight shift \cite{17} leads to asymmetrical form of each satellite line as well as central one. In Fig.\[1\] the NMR spectrum of Sc polycrystalline sample at liquid helium temperature ($T = 1.5K$) is shown. We were not able to observe all satellite lines. Namely the lines corresponding to the transitions $\frac{7}{2} \leftrightarrow \frac{5}{2}$ and $-\frac{5}{2} \leftrightarrow -\frac{7}{2}$ were not detected. It is connected with the sensivity of our apparatus as well as with the polycrystalline sample preparation. Only very careful preparation of metal filings allowed to observe all six satellite lines in a powder sample \cite{17}. It was shown in \cite{18} that the spacings between corresponding satellite pairs in NMR linshape in metals are unaffected by the anisotropic Knight shift through the second order of perturbation theory, and are also independent of the second-order quadrupole contributions:

$$\nu (-m + 1 \leftrightarrow -m) - \nu(m \leftrightarrow m - 1) = \left(m - \frac{1}{2}\right) \nu_Q,$$

(1)

where $\nu_Q = 3e^2gQ/2I(2I - 1)h$ is a convinient measure of the quadrupole interaction strength. Here $e$ is the charge of electron, $eQ$ is the electric quadrupole moment of the nucleus, $eq$ is the total electric field gradient at the nucleus, $I$ represents the angular momentum quantum number and $h$ is Planck’s constant. We obtained from our data $\nu_Q \approx 0.128 MHz$ that agrees well with the value $\nu_Q = 0.144 MHz$ reported in \cite{17} for polycrystalline sample, with the value $nu_Q = 0.124 MHz$ obtained in \cite{10} from nuclear resonance measurements.
at single crystal sample and with the value $\nu_Q = 0.13\, MHz$ measured in \cite{13} by nuclear quadrupole resonance method.

The $cw$ NMR of scandium is the first important step if one is going to provide the correct measurements of spin-lattice relaxation by using pulse NMR technique. Only in this case one can estimate the pulse duration for complete saturation of all transitions between nuclear energy levels. It is well known that NMR spectrum can be obtained by the Fourier transform of free induction decay (FID). In Fig.2 one can see FID signals of $^{45}Sc$ in single crystal at different frequencies (6.3, 4.71 and 3.65$MHz$). Obviously the scandium FID signal is complicated due to the interference with copper (containing in NMR coil wires) FID signal. The gyromagnetic ratio for copper is rather close to the corresponding value for scandium ($\gamma_{\frac{2\pi}{2\pi}} = 1.0348 kHz/Oe$ for $^{45}Sc$, $\gamma_{\frac{2\pi}{2\pi}} = 1.128 kHz/Oe$ for $^{63}Cu$ and $\gamma_{\frac{2\pi}{2\pi}} = 1.208 kHz/Oe$ for $^{65}Cu$), so the lowering of the external magnetic field leads to the overlapping of all signals.

\section{IV. RELAXATION.}

Successful observation of NMR in metallic single crystals is rather seldom because of skin effect. For example, the measurements of NMR in metallic $Tl$ \cite{19}, $Ga$ \cite{20}, $Al$ \cite{21}, $Sc$ \cite{10} samples can be mentioned. By using home made pulse NMR technique we have observed the spin echo in polycrystalline samples and single crystal in inhomogeneous applied magnetic field. The corresponding transverse magnetization decays are shown in Fig.3. It is seen that both decays have essential one-exponential character and the corresponding lineshapes have the Lorentz form. The difference in $T_2$ values can be attributed to the Knight shift dispersion in polycrystalline samples which leads to more longer value of transverse relaxation time. As mentioned above that for correct $T_1$ measurements it is very important to choose the pulse duration for the complete saturation of nuclear spin system. The Fig.4 illustrates how longitudinal relaxation time $T_1$ depends on pulse duration time. When we use long pulse duration time (the corresponding spectrum is more narrow) we saturate only some part of nuclear magnetic resonance spectrum. Consequently the measured $T_1$ is shorter because
of spectral diffusion processes and the relaxation has multi-exponential character (see [22] and Section 5). Naturally all our measurements have been provided by using the shortest pulse duration time. As in case of $T_2$ measurements the longitudinal magnetization decays have also one-exponential character. One see it in Fig.5 where longitudinal magnetization evolution were measured at three different frequencies (3.65$MHz$, 4.71$MHz$ and 6.3$MHz$).

The obtained values of $T_1$ in our experiments and the data known before [5]-[13] allowed us to plot the magnetic field dependence of the Korringa constant which is shown in Fig.6.

The obtained magnetic field dependence can be explained by two ways at least. They are the quenching of spin fluctuations by magnetic field and the impurity influence.

As far as the relaxation rate increasing with magnetic field decreasing is observed, first of all we can think about magnetic field influence on the spin fluctuations and work in the framework of self-consistent renormalization (SCR) theory [23]. Namely it is known from the heat capacity measurements that spin fluctuation is quenched at magnetic field above 5 T [14]. The spin-lattice relaxation rate of $^{45}Sc$ in intermetallic alloy $Sc_3In$ increases to almost five times when magnetic field goes down from 6.8$T$ to 0.8$T$ at low temperatures [15].

If we restrict ourselves by consideration only Fermi contact interaction between nuclear and electronic spins then the rate of the nuclear spin-lattice relaxation is determined by the following expression [24]:

$$T_1^{-1} = \gamma^2 A_{hf}^2 T \sum_{q} \frac{Im \chi^{+}(q, \omega_0)}{N^2 \omega_0},$$

where $A_{hf}$ describes the hyperfine interaction,

$$\chi^{+}(q, \omega) = i \int_0^\infty dt \cdot e^{i\omega t} \langle [S^-(q, t), S^+(-q, 0)] \rangle$$

is the transverse electronic dynamic susceptibility. It was assumed here that an external magnetic field as well as internal one are directed along $z$-axis. The calculations of $\chi^{+}(q, \omega)$ in the framework of SCR theory [25] lead to the formula for the Korringa constant [26]:

$$(T_1T)^{-1} = A + \frac{B \cdot M/H}{1 + C \cdot M^3/H},$$

(3)
which can be re-written in the form more convenient for the comparison with the experimental data:

\[(T_1 T)^{-1} = A + \frac{B \cdot \varsigma}{1 + C \cdot \varsigma^3 \cdot H^2},\]  \hspace{1cm} (4)

where \(\varsigma = M/H\). The values of parameters \(A\), \(B\) and \(C\) in equation (4) can be obtained from the behavior of the Korringa constant at different magnetic field. So, at high magnetic fields (see for example the experimental results in [11]) when one approaches to the magnetization saturation limit the contribution coming from the second term in equation 3 will be negligible and we get the value of parameter \(A\).

We should note here that equations 3 and 4 can not be applied for very low magnetic fields. The well-known Korringa relation has been obtained in the approximation when the interaction between nuclear spins is so small in comparison with the nuclear Zeeman energy. So it was possible to consider the energy levels for a given nuclear and to make corresponding calculations. At small magnetic fields one must consider the system of all nuclear spins and use some thermodynamic relations, for example, spin temperature concept. Such situation has been realized, for example, in the measurements of nuclear magnetic relaxation in Cu [27]. It was shown in [27] that at low magnetic fields (lower than local magnetic fields) magnetic impurity, such as \(Fe\), \(Cr\), \(Ni\), \(Mn\), can strongly influence the nuclear spin-lattice relaxation process.

It is important also that at small magnetic fields the effect of electron spin fluctuations can be partially washed out by effect of non-equal spacings between nuclear energy levels (for nuclei with quadrupole moments) and by nuclear spin-spin interactions.

It follows from above that as far as the impurity contents in Cornell’ group experiments [13] was approximately the same as in our one and these experiments were provided at zero magnetic field (nuclear quadrupole resonance measurements) we must exclude the Cornell data from our analysis and from the Fig.6.

Generally speaking for the fitting procedure it is necessary to have the magnetic field dependence of \(\varsigma\) parameter which is magnetization divided by value of the applied magnetic
field. The special experiments at liquid helium temperature with use the SQUID give us the necessary data shown in Fig.4. The magnetic field dependence of $\zeta$ parameter is not so strong and can be described by exponential function:

$$\zeta = a_1 + b_1 \cdot \exp\left(-\frac{c_1}{H}\right)$$  \hspace{1cm} (5)

as well as by function similar to the pointed out one in equation 4:

$$\zeta = a_2 + \frac{b_2}{1 + c_2 H^2}.$$  \hspace{1cm} (6)

The results of these fittings are presented in Fig.4 and in Table 2. Any from the functions 5 and 6 can be used in the fitting procedure for the equation 4. The result of this fitting is shown by solid line in Fig. 6. Of course, the agreement between experimental points and the theory quantitatively is not so good because of rather big differences between the experimental points obtained by different group. But the tendency to the magnetic relaxation rate increasing at low magnetic field can be attributed in part to the spin fluctuation quenching.

The another possible reason for the observed increasing is the impurity influence (see the impurity contents in Section 2). The magnetic field dependence of spin-lattice relaxation time can arise from magnetic impurities influence. Scandium like palladium is an exchange enhanced metal and its magnetic properties are very sensitive to $3d$ impurities. The giant magnetic moments associated with $Fe$ impurities in a $Pd$ matrix have been observed and their ground state has been investigated in [28]. In the case of scandium there is also possibility for the enhancement of impurity magnetic moments by exchange interactions. The magnetic impurity effect on the magnetic property of $Sc$ metal were discussed in [29] where the observed anomalies below $1mK$ in magnetic susceptibility and magnetization have been explained as the spin glass phenomena. It is well known that the magnetic impurities contribution to the nuclear spin-lattice relaxation rate is proportional to $(1 - p_0^2)$, where $p_0$ represents the equilibrium magnetic polarization of impurity and for two-level system is equal to $\tanh\left(\frac{mH}{k_B T}\right)$. Here $k_B$ is the Boltzman constant, $T$ is temperature and $m$ stands for
the magnetic moment of impurity atom. The dashed line in Fig.6 shows the results of fitting when one takes into account two contributions to the magnetic relaxation rate - the magnetic field independent contribution coming from Korringa mechanism and the contribution from the magnetic impurities. The value of the impurity magnetic moment obtained in this fitting procedure is equal approximately to $8\mu_B$ that two times bigger than estimations of effective magnetic moment of iron impurity in scandium metal [29]. From this point of view we could conclude that one has to take into account the all possible mechanisms for magnetic field dependence of nuclear spin-lattice relaxation in scandium metal. But we should mention here that the proportionality of the relaxation rate to $(1 - p_0^2)$ means that Korringa constant also should be temperature dependent. Accordingly to SCR theory at temperature well above transition temperature into ordered state in electron system the nuclear relaxation rate $T_1^{-1}$ is approximately proportional to $T\chi$. The susceptibility of Sc changes a small value with temperature. So it seems reasonably to think that most dominant field dependence of the Korringa constant comes from spin fluctuations. Additional measurements at lower temperatures help to eliminate the influence of spin fluctuations.

V. THE POSSIBLE SOURCES OF NON-EXPOENTIAL RELAXATION

As it was mentioned above the $^{45}$Sc NMR spectrum consists of seven unequally spaced lines: the central line at $\omega_0$ corresponding to the transition $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ and six satellite lines $m \leftrightarrow m - 1$. This spectrum is rather wide. For example, at magnetic field $1.483T$ (the corresponding frequency is $15.33MHz$) the frequencies for the most right and most left satellite lines are distinguished on the value from $0.5MHz$ to $0.8MHz$ in the dependence on magnetic field orientaion with respect to crystallographic axis c. This enormous width of the nuclear resonance leads to some difficulties in the usual pulse NMR experiments in which the recovery of the nuclear magnetization is observed after application of a saturating "comb" of radiofrequency pulses. It is very difficult to achieve the complete saturation of spin-system (i.e. to equalize the populations of all nuclear spin levels) due to a big
discrepancies in the resonant frequencies for the transitions $m \leftrightarrow m - 1$ (for the system of unequally spaced levels the simultaneous nuclear spin-flips involving two different transitions are forbidden by energy conservation requirements [30]). The question about the influence of the incomplete saturation of spin system on the nuclear magnetization recovery in the case of two isotopes of titanium ($^{47}Ti$, $I = \frac{5}{2}$ and $^{49}Ti$, $I = \frac{7}{2}$) has been investigated in [22]. Here we report only about the results of our numerical calculations. In Fig.8 the curves of magnetization recovery are shown at different initial conditions. We assume here for the numerical calculation purposes the nuclear spin-lattice relaxation time being equal to 600 msec. The curve 1 in Fig.8 corresponds to the case when only central transition $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ is saturated while the other levels have the equilibrium populations. The curve 2 is obtained for the case when a comb of sufficient duration is used in order to allow the populations of the $|m| > \frac{1}{2}$ levels to attain the thermal equilibrium with those of the $|m| = \frac{1}{2}$ levels. In other words, just after the comb the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition is saturated, while the population differences between all other pairs of adjacent levels are determined by the lattice temperature. Finally the curve 3 represents the single exponential relaxation observed when all transitions are saturated at initial time.

But as we will show now the incomplete saturation of NMR line because of its enormous width is not onest source for the multiexponential relaxation in Sc metal. In order to observe single exponential relaxation it is necessary to saturate completely nuclear spin system by the comb. But at the same time the new effect connected with the system of conduction electrons can appear. Usually, in order to escape the skin-effect manifestations the NMR experiments in metals are provided with polycrystalline samples and the crystalline particles are covered by the paraffin for the isolation each particle from others. If we keep in mind that in the NMR experiments at liquid helium temperatures such paraffin layer might make difficult the heat exchange between powder particles and helium bath. So the conduction electron system being the thermal reservoir for nuclear spin system can have the temperature difference from the helium bath one just after a comb. The elementary calculations of the phonon contribution to the molar heat capacity of Sc metal accordingly to the Debye’s
model (Debye temperature $\Theta_D = 352.2 K$ [31])

$$C_{ph} = \frac{12\pi^4}{5} Nk_B \left( \frac{T}{\Theta_D} \right)^3$$

(7)

and the electron contribution

$$C_{el} = \gamma_e T,$$

(8)

$C_{el} = \gamma_e T$, where $\gamma_e = 10.38 mJ/mol \cdot K^2$ [31], give us the values listed in Table 3.

One can see that the phonon heat capacity is so small to thermalize the conduction electron system at these temperatures and other thermal reservoir is necessary, for example, the helium bath. The effects of the taking into account the finite phonon heat capacity in the nuclear spin-lattice relaxation problems were considered during many years [32]- [34]. In this section we shall not discuss in the details of the mechanism of energy transfer from the conduction electrons to the helium bath (is this path by the phonons in scandium crystal lattice or not, how the paraffin layer effects on this path and so on). We shall consider only phenomenologically the heat exchange between conduction electrons and the helium bath in the following two particular cases:

a) The ”usual” heat exchange, when the heat flow from conduction electrons to liquid helium is proportional to the difference between their temperatures;

b) The heat exchange of the ”Kapitza resistance” type, when the heat flow is proportional to the difference of the fourth powers of their temperatures.

In Fig.9 the simplified scheme of the thermal reservoirs and heat flows taking place in the problem of nuclear magnetic relaxation in metals is shown. $Q_1$ and $Q_2$ represent the amounts of heat coming to the nuclear spin system and the conduction electron system respectively from the radiofrequency pulses saturating nuclear spin system.

After a comb the heat flows in the considered system can be described by the following kinetic equations:

$$\frac{dQ_n}{dT} = C_n \frac{dT_n}{dt} = -\alpha (T_n - T_{el})$$

(9)
\[ \frac{dQ_{el}}{dt} = C_{el} \frac{dT_{el}}{dt} = -\beta (T_{el} - T_0) - \alpha'(T_{el} - T_n) \quad \text{case a)} \quad (10) \]

\[ \frac{dQ_{el}}{dt} = C_{el} \frac{dT_{el}}{dt} = -\beta'(T_{el}^4 - T_0^4) - \alpha'(T_{el} - T_n) \quad \text{case b)} \quad (11) \]

Here \( \alpha, \alpha', \beta, \beta' \) are the kinetic parameters, \( T_n, T_{el} \) and \( T_0 \) are the temperatures of nuclear spin system, conduction electron system and liquid helium correspondingly. As far as the heat capacity of the nuclear spin-system is very small in comparison with the conduction electron one at liquid helium temperature we can neglect the second term in the equations \( (10), (11) \). The given equations can be re-written in the more convenient form by introducing the inverse temperatures of systems - \( \beta_n, \beta_{el}, \beta_0 \) for nuclear spin system, conduction electron system and liquid helium correspondingly - and the dimensionless quantity \( m \) and \( n \):

\[ m = 1 - \beta_n/\beta_0 \quad \text{and} \quad n = 1 - \beta_{el}/\beta_0 \quad (12) \]

We should take into account also that the heat capacity of the conduction electrons depends on temperature linearly. The final system of kinetic equations looks as follows:

\[ \frac{dm}{dt} = \frac{1}{\tau_{nel}} \frac{n - m}{1 - n} \quad \text{case a)} \quad (13) \]

\[ \frac{dn}{dt} = -\frac{n}{\tau_{el0}} \]

\[ \frac{dm}{dt} = \frac{1}{\tau_{nel}} \frac{n - m}{1 - n} \quad \text{case b)} \quad (14) \]

\[ \frac{dn}{dt} = -\frac{1}{\tau_{el0}} \frac{1 - (1 - n)^4}{1 - n^2} \]

In order to obtain the temporal dependence of the nuclear magnetization it is necessary to find the time dependence of the quantity \( m(t) \) from \((13)\) or \((14)\) and then take into account that nuclear magnetization \( M \) is proportional to the inverse nuclear spin temperature \( \beta_n \) (Curie law). The non-linear systems of kinetic equations \((13)\) and \((14)\) can be solved numerically for the different values of the kinetic parameters \( \tau_{nel}, \tau_{el0} \) and \( \tau'_{el0} \) and initial deviations of...
the conduction electron temperature from the equilibrium meaning (the initial value of the parameter \( n \)). The results of some numerical solutions for the time evolution of the quantity \( m(t) \) are given in Fig.10 and Fig.11. As the result of calculation we see that due to the heating of the conduction electron system by radiofrequency pulses the nuclear magnetic relaxation has essentially non-single exponential character.

VI. CONCLUSION.

The nuclear magnetic relaxation in scandium metal was investigated at liquid helium temperature for both single crystal and powder samples. The obtained temperature and field dependence of the Korringa constant can be described by the means of the spin fluctuation theory. It was shown the most probable reason for the high field decreasing of the relaxation rate is the quenching of spin fluctuations. The other possible reason - the magnetic impurity influence - was also considered. The reasons of the existing variations of the Korringa constant were discussed. The possible sources of non-single exponential relaxation were investigated.
TABLES

TABLE I. The values of the Korringa constant obtained from NMR experiments at different conditions

| Sample, purity | Temperature, $K$ | Frequency, MHz | Magnetic field, $T$ | $T_1 T$, sec $\cdot K$ | Ref. |
|----------------|------------------|----------------|---------------------|------------------------|------|
| polycrystalline, 99.9% | 1.7 ± 300 | 14.5 | 1.4 | 0.6 | [5] |
| | 1.5 ± 77.0 | 10.0 | 0.967 | 0.11 | [5] |
| single crystal, 99.9% | 77.0 | 8.0 | 0.77 | $(1.25 - 0.58 \sin^2 \theta)^{-1}$ | [8] |
| polycrystalline | 1.0 ± 4.0 | 17.0, 30.0 | 1.64, 2.89 | 1.3 ± 0.2 | [9, 12] |
| polycrystalline, 99.98% | 1.5 ± 77.0 | 10.0 | 0.967 | 1.5 ± 0.2 | [9] |
| single crystal, cos $\theta = 1$ | 77 | 8.0 | 0.77 | 0.81 | [10] |
| single crystal, cos $\theta = 0$ | 77 | 8.0 | 0.77 | 1.49 | [10] |
| single crystal, cos $\theta = 1/\sqrt{3}$ | 4.2 | 8.0 | 0.77 | 1.1 ± 0.1 | [10] |
| polycrystalline | 300 | 12.0 | 1.16 | 1.2 ± 0.1 | [10] |
| | 1.3 ± 300 | 50.0 | 4.82 | 1.6 | [11] |
| | 1.3 ± 4.2 | 20.0 | 1.93 | 1.48 | [11] |
| | 1.3 ± 4.2 | 5.0 | 0.48 | 1.36 | [11] |
| | 0.003 ± 0.01 | 0.39, 0.26 | 0 (NQR) | 0.09 ± 0.009 | [13] |
### TABLE II. The fitting parameters for the measurements of $M/H$

| Orientation of the external magnetic field | Eq. $5$ | Eq. $6$ |
|------------------------------------------|---------|---------|
|                                          | $a_1, \text{emu/g}$ | $b_1, \text{emu/g}$ | $c_1, T$ | $a_2, \text{emu/g}$ | $b_2, \text{emu/g}$ | $c_2, T^{-2}$ |
| along $a$-axis                          | $8.18 \cdot 10^{-6}$ | $1.14 \cdot 10^{-6}$ | $0.99$ | $8.17 \cdot 10^{-6}$ | $1.04 \cdot 10^{-6}$ | $1.70$ |
| along $c$-axis                          | $7.75$ | $1.47$ | $1.24$ | $7.75$ | $1.33$ | $1.05$ |

### TABLE III. The phonon and electronic heat capacities at low temperatures in $^{45}$Sc

| $T, K$ | $C_{ph}, 10^{-3} \text{J/(K \cdot mol)}$ | $C_{el}, 10^{-3} \text{J/(K \cdot mol)}$ |
|--------|------------------------------------------|------------------------------------------|
| 4.2    | 3.1                                       | 44.9                                     |
| 1.5    | 0.14                                      | 16.1                                     |
FIGURES

FIG. 1. CW $^{45}Sc$ NMR spectrum ($\nu = 5.113\text{MHz}$) in polycrystalline sample at liquid helium temperature.

FIG. 2. Free induction decay of $^{45}Sc$ signals at $T = 1.5K$. The frequencies and pulse durations are shown.

FIG. 3. The transverse magnetization decays for Sc single crystal and polycrystalline samples.

FIG. 4. The dependencies of $^{45}Sc$ nuclear longitudinal relaxation time on the pulse duration time at $T = 1.5K$. The resonance frequencies are shown.

FIG. 5. The recovery of the longitudinal magnetization in pulse $^{45}Sc$ NMR experiments with single crystal at $T = 1.5K$. The pulse duration time $\tau = 1\mu s$.

FIG. 6. The magnetic field dependence of the Korringa constant. The data known from the literature as well as our data are shown. The solid line represents the result of the fitting procedure by use Eq.3. The dashed line is drawn with taking into account the magnetic impurity influence (see text).

FIG. 7. The magnetic field dependence of the parameter $\zeta$. The solid and dashed lines show the fitting by use Eq. 3 and Eq. 5 correspondingly.

FIG. 8. The time evolution of nuclear magnetization at different initial saturation. The nuclear spin-lattice relaxation time is shown.

FIG. 9. The thermal reservoirs and heat flows in the system under consideration.
FIG. 10. The time evolution of $m(t)$. The open symbols correspond to the case of the ”usual” heat exchange, whereas the solid ones correspond to the ”Kapitza resistance” type of the heat exchange. The kinetic parameters are the following: $\tau_{nel} = 1\, \text{sec}$, $\tau_{el0} = \tau'_{el0} = 2\, \text{sec}$. The initial conditions for the electron system are shown in the frame. The nuclear spin system is completely saturated at initial time.

FIG. 11. The same as in Fig. 10. $\tau_{el0} = \tau'_{el0} = 10\, \text{sec}$. 
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\( \nu = 6.3 \text{MHz} \)
\( \tau_{\text{puls}} = 1 \mu\text{s} \)

\( \nu = 4.71 \text{MHz} \)
\( \tau_{\text{puls}} = 1.2 \mu\text{s} \)

\( \nu = 3.65 \text{MHz} \)
\( \tau_{\text{puls}} = 1 \mu\text{s} \)
$45^{\text{Sc}}$ polycrystalline

$T = 4.2 \text{K}; \quad \nu = 4.86 \ \text{MHz}$

$\tau_{\text{puls}_1} = 1.5 \ \mu s$

$\tau_{\text{puls}_2} = 1.5 \ \mu s$

$A(t) = A_0 \exp(-t/T_2)$

$A_0 = (61.7 \pm 0.9)$

$T_2 = (276 \pm 3) \ \mu s$

$45^{\text{Sc}}$ single crystal

$T = 1.5 \text{K}$

$\tau_{\text{puls}_1} = 2.6 \mu s$

$\tau_{\text{puls}_2} = 1 \mu s$

$A(t) = A_0 \exp(-t/T_2)$

$A_0 = (71 \pm 4)$

$T_2 = (146 \pm 7) \ \mu s$
\[ \nu = 3,65 \text{MHz} \]
\[ T_1 = (576 \pm 19) \text{ms} \]

\[ \nu = 4,71 \text{MHz} \]
\[ T_1 = (639 \pm 19) \text{ms} \]

\[ \nu = 6,3 \text{MHz} \]
\[ T_1 = (775 \pm 10) \text{ms} \]
Our data from [10] and data from [9] are plotted on the graph. The fitting line represents the SCR theory, while the dotted line represents the fitting line for magnetic impurities.
Magnetic field, T

Parameter $\zeta$, $10^{-6}$ emu/g

- a-axis
- c-axis
The graph represents the normalized magnetization $M(t)/M^0$ over time, with $T_1 = 600$ msec.
Nuclear spins

Conduction electrons

Helium bath

\[ \frac{Q_1}{Q_2} \]

\[ \text{time } t, \text{ sec} \]

\[ n(0) = 0.05 \]

\[ n(0) = 0.1 \]

\[ n(0) = 0.2 \]
