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NUCLEAR MAGNETIC RELAXATION IN SCANDIUM 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 dependencies of the Korringa constant can be described by means of the spin fluctuation theory for $3d$ electrons. It is shown that the most probable reason for the decreasing relaxation rate at high magnetic field is the quenching of spin fluctuations. Another possible reason – the influence of magnetic impurities – is also analyzed. We discuss the reasons for the experimentally observed variations of the Korringa constant. The possible sources of non-single-exponential relaxation in scandium metal are investigated.

Introduction

The interest for investigations of the behavior of the nuclear spin system in scandium ^{45}Sc ($I = 7/2$) metal is motivated by two main reasons. First of all, scandium is a transition metal, which has only one $3d$ electron. Among other transition metals, possessing unique magnetic properties due to their $3d$ electrons, scandium is, probably, less understood, although, in principle, with only one d electron it might be expected one of the best understood. The reason is in great difficulty, up to recent years [1], to obtain impurity-free scandium metal, especially with respect to the iron content.

Second, 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 small value of Korringa constant the nuclear spin-relaxation time is so short, that the temperature of conduction electrons and the temperature of nuclear spins are practically equal during an experiment. It means that the exchange interaction between nuclear spins is rather strong that should lead to rather high temperatures of nuclear ordering (the order of μK, while in such metals as Cu, Ag and Rh the corresponding temperatures have the order of few nK and even of hundreds pK [4]). Besides the knowledge of the parameters of nuclear spin system nuclear magnetic resonance (NMR) yields information about conduction electron subsystem, which is hardly deduced from band structure calculations. In particular, the core electrons and the valence electrons give distinct contributions to the Knight shift and nuclear magnetic relaxation time. This motivates the importance of precise determination of nuclear spin-lattice relaxation time from evolution of nuclear longitudinal magnetization.

There are rather few NMR investigations of Sc metal in the temperature range $0.001 \div 300$ K [5–11]. They give rather different values for the Korringa constant K (from 0.09 c$\cdot$K to 1.6 c$\cdot$K) in the dependence on experimental conditions, particularly on the applied magnetic fields (see Table 1). It should be noted that in zero magnetic

Table 1. Korringa constant values obtained in NMR measurements at different conditions

Sample, purity and angle θ between magnetic field and crystal c-axis	Temperature, K	Frequency, MHz	Magnetic field, T	T_1T, s·K	Ref.
powder, 99.9%	1.7÷300	14.5	1.4	0.6	5
	1.5÷77	10.0	0.967	0.11	6
single crystal, 99.9%, θ	77.0	8.0	0.77	$(1.25 - 0.58\sin^2\theta)^{-1}$	8
powder	1.0÷4.0	17.0	1.64	1.3±0.2	7
		30.0	2.89	1.3±0.2	12
powder, 99.98%	1.5÷77	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	
single crystal, $\cos\theta = 1/\sqrt{3}$	4.2	8.0	0.77	1.1±0.1	
powder	300	12.0	1.16	1.2±0.1	
powder	1.3÷300	50.0	4.82	1.6	11
powder	1.3÷4.2	20.0	1.93	1.48	
powder	1.3÷4.2	5.0	0.48	1.36	
single crystal foil	0.003÷0.01	0.39, 0.26	0 (NQR)	0.09±0.009	13

field (nuclear quadrupole resonance investigations [13]) the value of the Korringa constant, obtained from the longest magnetization decay, is extremely low, namely 0.09 c·K. *A priori* it might be expected that magnetic field dependence of the Korringa constant could be explained as the result of the influence of spin fluctuations. It is well known that the specific heat at high magnetic fields is decreased because of spin fluctuation quenching [14]. Such behavior for nuclear magnetic relaxation was observed for Sc intermetallic alloys [15]. However, in the case of pure Sc metal there is no information about influence of spin fluctuations on the nuclear spin system. It should be noted here that the recent theoretical calculations of spin relaxation times and susceptibilities, based on magnetic correlation functions [16], showed the importance of Fermi surface effects 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 obtained in the different experiments.

The motivation for a study of nuclear magnetic relaxation in scandium metal is to shed light on behavior of ^{45}Sc nuclear spin system. We focus our main interest on the reasons for observed magnetic field dependence of the Korringa constant as well as on the possible sources for non-exponential relaxation.

The paper is organized as follows. After short description of our samples given in the next section we report the results of continuous wave NMR measurements in Sec. 2. Sec. 3 deals with results of pulse NMR measurements and discussions of magnetic field dependence of Korringa constant. In Sec. 3 the possible sources for non-exponential nuclear magnetic relaxation in scandium metal are studied theoretically. The paper is concluded in Sec. 4.

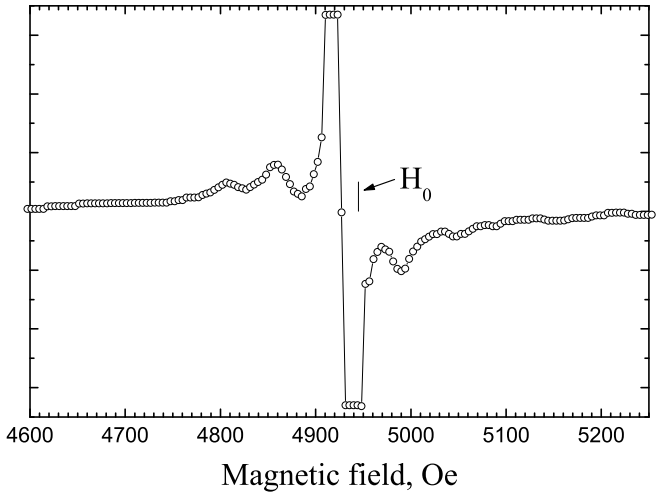

Fig. 1. *cw* ^{45}Sc NMR spectrum ($\nu = 5.133$ MHz) in powder at liquid helium temperature. The position of the resonant field is shown

1. 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 $3.5 \times 2.0 \times 27$ 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.

2. Continuous wave 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 [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 ($T = 1.5$ K) is shown.

We were not able to observe all satellite lines. Namely the lines corresponding to the transitions $7/2 \leftrightarrow 5/2$ and $-5/2 \leftrightarrow -7/2$ were not detected. The reason is the sensitivity of our apparatus as well as the polycrystalline form of sample. Only very careful preparation of samples allowed to observe all six satellite lines in a powder sample [17]. It was shown in [18] that the spacings between corresponding satellite pairs in NMR lineshape in metals are unaffected by the anisotropic Knight shift in the second order of perturbation theory, and are also independent of the second-order quadrupole contributions:

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

where $\nu_Q = 3e^2qQ/2I(2I-1)h$ is a convenient 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 denotes the angular momentum quantum number and h is the 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 [17] for the polycrystalline sample, with the value $\nu_Q = 0.124$ MHz obtained in [10] from nuclear

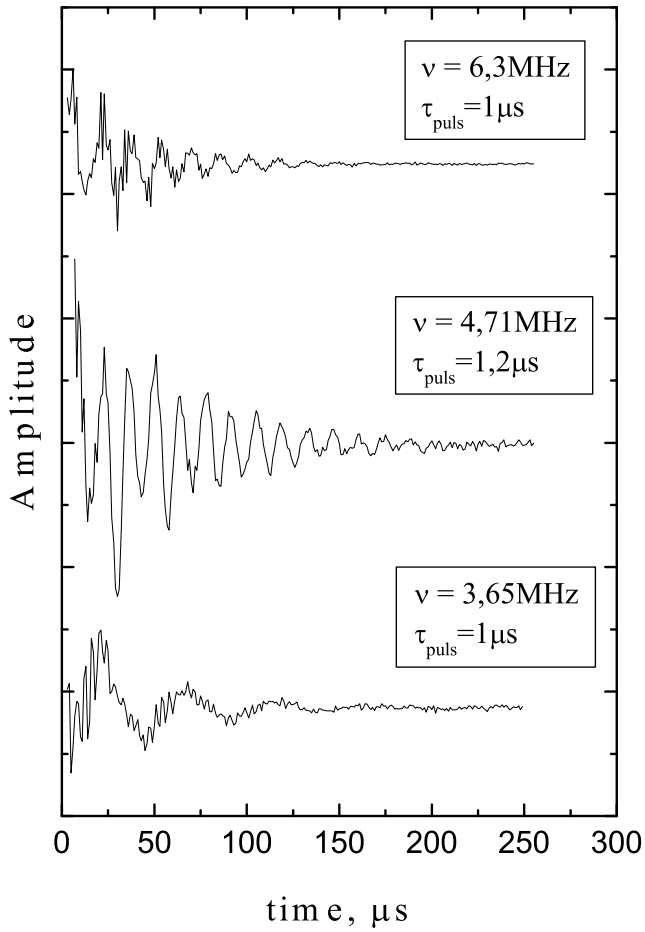

Fig. 2. ^{45}Sc free induction decay at $T = 1.5$ K. The corresponding frequencies and pulse durations are shown in frame

resonance measurements at single crystal sample and with the value $\nu_Q = 0.13$ MHz measured in [13] by nuclear quadrupole resonance method.

The continuous wave (*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. Using *cw* NMR 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 a 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 signal, coming from NMR coil wires. The gyromagnetic ratio of copper is rather close to corresponding value of scandium ($\gamma/(2\pi) = 1.0348$ kHz/Oe for ^{45}Sc, $\gamma/(2\pi) = 1.128$ kHz/Oe for ^{63}Cu and $\gamma/(2\pi) = 1.208$ kHz/Oe for ^{65}Cu), so the lowering of the external magnetic field leads to overlapping of all signals.

3. ^{45}Sc nuclear magnetic relaxation

3.1. Transverse and longitudinal relaxation measurements. Successful observation of NMR in metallic single crystals is rather seldom because of skin effect. For

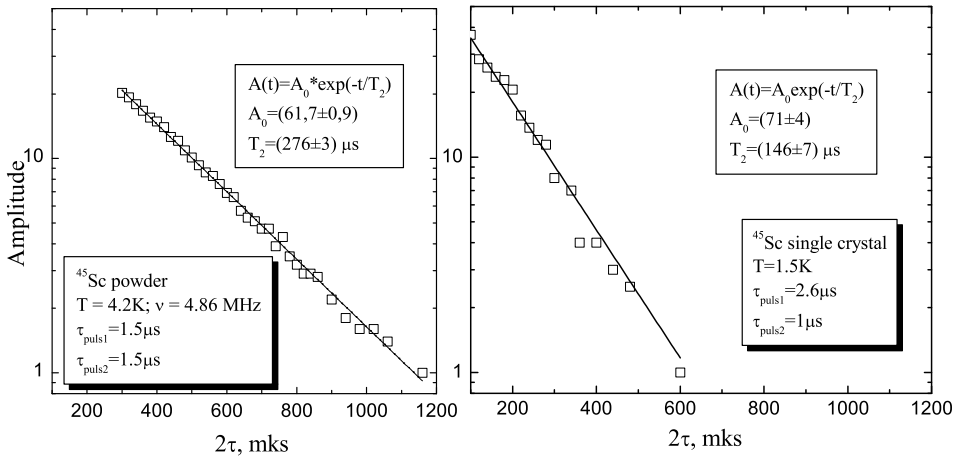

Fig. 3. ^{45}Sc transverse magnetization decays in single crystal and powder at liquid helium temperature. The pulse durations are shown in lower frames. In both cases the transverse magnetization decays are described by single exponential function. Solid lines correspond to the fitting with single exponential function with parameters shown in the upper frames

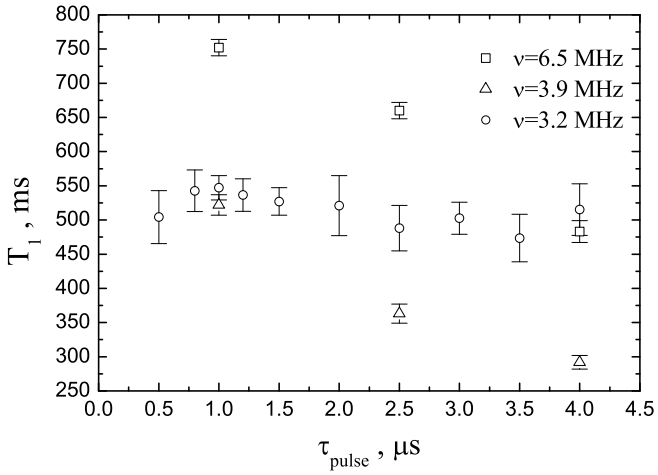

Fig. 4. Dependence of ^{45}Sc nuclear longitudinal relaxation time on the pulse duration time at temperature 1.5 K. The NMR frequencies are listed

example, the measurements of NMR in metallic Tl [19], Ga [20], Al [21], Sc [10] samples can be mentioned. 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 single 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 a longer value of transverse relaxation time. As was mentioned above, 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 T_1 dependence 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

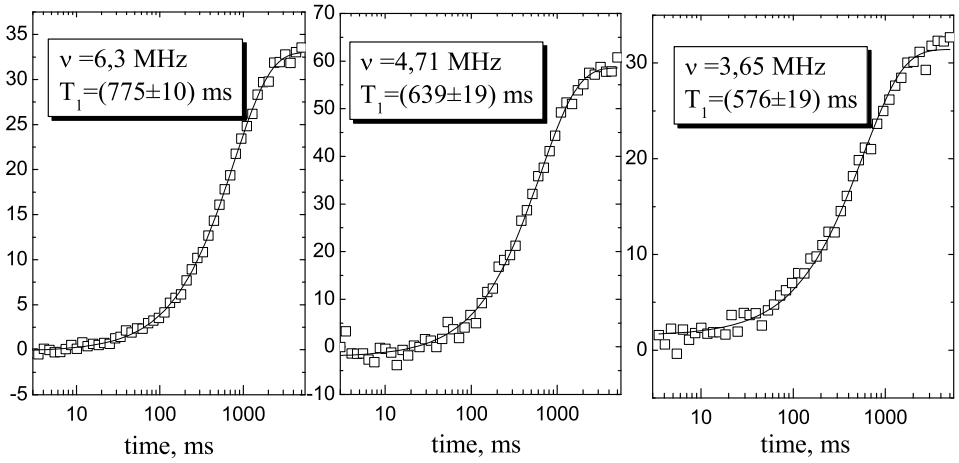

Fig. 5. The evolution of ^{45}Sc nuclear longitudinal magnetization in different magnetic fields at temperature 1.5 K. The NMR frequencies are listed

shorter because of spectral diffusion processes, and the relaxation has multi-exponential character (see [22] and Sec. 4). Naturally, all our measurements have been performed using the shortest pulse duration time. As in case of T_2 measurements the longitudinal magnetization decays have also single-exponential character. One can see it in Fig. 5, where longitudinal magnetization evolution is presented for 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 at least in two ways. They are the magnetic influence on spin fluctuations in electron subsystem, and the dependence of impurity magnetization on applied magnetic field.

3.2. The quenching of spin fluctuations. As far as the relaxation rate increases with decreasing of magnetic field is observed, we can think first of all about the quenching of spin fluctuations by magnetic field and apply the formalism 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 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]:

$$T_1^{-1} = \gamma^2 A_{hf}^2 T \frac{\sum_q \mathrm{Im}\left[\chi^{-+}(q,\omega_0)\right]}{N^2\omega_0}, \tag{2}$$

where A_{hf} describes the hyperfine interaction,

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

is the transverse electronic dynamic susceptibility. It was assumed here that an external magnetic field as well as internal one are directed along the z-axis. The calculations of

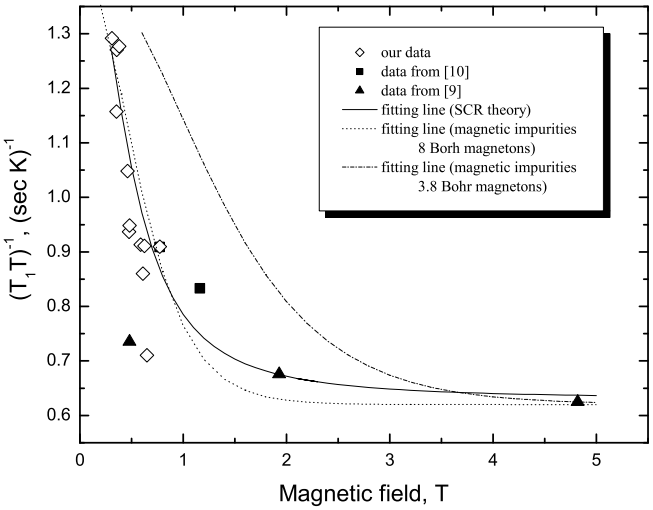

Fig. 6. Magnetic field dependence of Korringa constant. The data known before as well as our data are shown. The solid line represents results of fitting procedure (Eq. (3)). The dash line shows the results of fitting with taking into account spin fluctuation effect as well as impurity influence (see Sec. 3.2)

$\chi^{-+}(q,\omega)$ in the framework of SCR theory [25] lead to the formula for the Korringa constant [26]:

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

which can be rewritten in more convenient form for the comparison with the experimental data:

$$(T_1T)^{-1} = A + \frac{B \cdot \varsigma}{1 + C \cdot \varsigma^3 \cdot H^2}, \tag{4}$$

where $\varsigma = M/H$. The values of parameters A, B and C in Eq. (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 the magnetization saturation limit, the contribution coming from the second term in Eq. (3) will be negligible, and we get the value of parameter A.

We should note here that Eqs. (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 small compared to the nuclear Zeeman energy. So it was possible to consider the energy levels for the isolated nucleus and to make corresponding calculations. At small magnetic fields one should 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 the influence of non-equal spacings between nuclear energy levels (for nuclei with quadrupole moments), and by nuclear spin-spin interactions.

It follows from the above that as far as the impurity contents in Cornell' group experiments [13] was approximately the same as in ours, and these experiments were

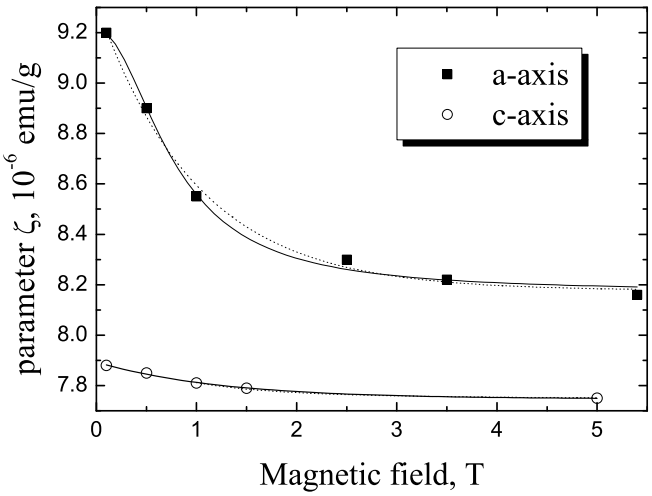

Fig. 7. Magnetic field dependence of the parameter ζ (see Eq. (4)). Solid and dash lines represents the results of fitting with use Eqs. (5) and (6) correspondingly

provided at zero magnetic field (nuclear quadrupole resonance measurements) we have to exclude the Cornell data from our analysis of the influence of spin fluctuation quenching on Korringa constant and from the Fig. 6.

Generally speaking for the fitting procedure it is necessary to have the magnetic field dependence of ς parameter which is, in fact, magnetization divided by value of the applied magnetic field. The SQUID measurements at liquid helium temperature give us the necessary data shown in Fig. 7. Magnetic field dependence of ζ parameter is not so strong and can be described by the exponential function:

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

as well as by function similar to the pointed out one in Eq. (4):

$$\zeta = a_2 + \frac{b_2}{1 + c_2 H^2}. \tag{6}$$

The results of these fittings are presented in Fig. 7 and in Table 2.

Both 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 (the difference in the fitting results with use the function (5) or (6) is negligible so only one solid line is presented in Fig. 6). Of course, the quantitative agreement between experimental points and the theory is not so good, because of rather big difference between the experimental points obtained by different group. However, qualitative tendency for the magnetic relaxation rate to increase at low magnetic field allows us to refer this behavior, at least in part, to the spin fluctuation quenching.

3.3. Impurity influence. Another possible reason for the observed increasing of relaxation rate at lower fields is the influence of impurities. 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 by Pobell' group [28]. In the case of scandium there is also possibility for the enhancement of impurity magnetic

Table 2. The fitting parameters for Eqs. (5) and (6)

Magnetic field	Eq. (5)			Eq. (6)		
	a_1, emu/g	b_1, emu/g	c_1, T	a_2, emu/g	b_2, 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

moments by exchange interactions. Magnetic impurity effect on the magnetic property of Sc metal was discussed in [29], where the observed anomalies below 1 mK in magnetic susceptibility and magnetization have been explained by the spin glass behavior. 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 is the equilibrium magnetic polarization of impurity. For a two-level system it is equal to $\tanh[(mH)/(2k_BT)]$.Here k_B is the Boltzmann constant, T is temperature and m stands for the magnetic moment of impurity atom. The dash 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 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 is in a reasonable range and 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 all possible mechanisms for magnetic field dependence of nuclear spin-lattice relaxation in scandium metal – the quenching of spin fluctuations as well as the impurity influence. However, the proportionality of the relaxation rate to $(1-p_0^2)$ in the case of taking into account only impurity influence means that the production T_1T also should be temperature dependent. From another point of view accordingly to SCR theory at temperature well above the magnetic ordering temperature nuclear relaxation rate T_1^{-1} is approximately proportional to $T\chi$. At these conditions the scandium electron susceptibility χ changes a little with temperature [29]. So it seems reasonably to think that most dominant field dependence of the Korringa constant comes from spin fluctuations. Additional measurements at lower temperatures can help to eliminate the influence of spin fluctuations.

4. Possible sources of non-exponential relaxation in scandium

4.1. The influence of incomplete saturation. As it was mentioned above, ^{45}Sc NMR spectrum consists of seven unequally spaced lines: the central line at ω_0 corresponds to the transition $+1/2 \leftrightarrow -1/2$, and six satellite lines correspond to $m \leftrightarrow m-1$. The spectrum is rather wide, at magnetic field 1.483 T (corresponding frequency is 15.33 MHz) the overall splitting of NMR spectrum changes from 0.5 MHz to 0.8 MHz, depending on the magnetic field orientation 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 applying the saturating "comb" of radio-frequency pulses. It is difficult to achieve complete saturation of the spin-system (i. e. to equalize the populations of all nuclear spin levels) because of big difference 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, $I = 5/2$ and ^{49}Ti, $I = 7/2$) has been investigated in [22].

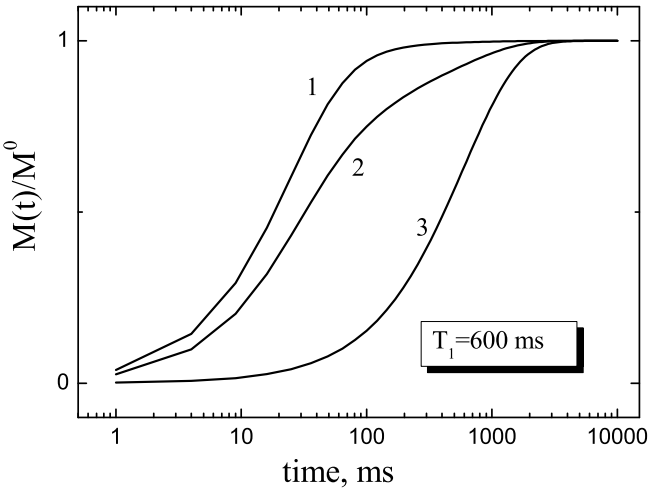

Fig. 8. The nuclear magnetization evolution at different initial levels of saturation of ^{45}Sc NMR spectrum (see text for detailed explanations). For numerical calculation the nuclear relaxation time has been chosen equal to 600 ms

Here we report only 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 ms. The curve 1 in Fig. 8 corresponds to the case when only central transition $1/2 \leftrightarrow -1/2$ is saturated, while the other levels have 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 $|m| > 1/2$ levels to attain the thermal equilibrium with those of the $|m| = 1/2$ levels. In other words, just after the comb the $1/2 \leftrightarrow -1/2$ 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.

Our results of longitudinal relaxation measurements presented in Fig. 5 are well described by single exponential function (see solid lines in Fig. 5) so we can conclude that by choosing the shortest pulse duration time we escape the influence of incomplete saturation on the form of relaxation curves.

4.2. The overheating of electron system by rf-pulses. Now we would like to show that the incomplete saturation of NMR line because of its enormous width is not the unique source for the multi-exponential relaxation in Sc metal. In order to observe single exponential relaxation it is necessary to saturate completely nuclear spin system by the comb. At the same time the new effect appears, which involves the conduction electron system. Usually, in order to escape the skin-effect manifestations, NMR experiments in metals are provided with powder samples, and the crystalline particles are covered by the paraffin to isolate them from others. Then we have to keep in mind that in NMR experiments at liquid helium temperatures such paraffin layer may introduce bottleneck in the heat exchange between powder particles and helium bath. So, just after a comb, the conduction electron system, being the thermal reservoir for nuclear spin system, can have a temperature different from the helium bath. Calculations of the phonon contribution to the molar heat capacity of Sc metal

Table 3. Phonon and electron heat capacities at low temperatures for scandium metal (see Eqs. (7) and (8))

Temperature, K	C_{ph}, 10^{-3} J/(K · mol)	C_{el}, 10^{-3} J/(K · mol)
4.2	3.1	44.9
1.5	0.14	16.1

accordingly to the Debye's model (Debye temperature $\Theta_D = 352.2$ K [31])

$$C_{ph} = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\Theta_D}\right)^3 \tag{7}$$

and the electron contribution

$$C_{el} = \gamma_e T, \tag{8}$$

where $\gamma_e = 10.38$ mJ/mol · K^2 [31], give us the values listed in Table 3.

One can see that the phonon heat capacitance is insufficient to drive the conduction electron system into thermal equilibrium state at these temperatures, and other thermal reservoir is necessary, for example, the helium bath. The effects of finite phonon heat capacity in the nuclear spin-lattice relaxation problems were investigated during many years [32–34]. In this section we will not discuss in details the mechanism of energy transfer from the conduction electrons to the helium bath, but we consider 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 for 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 from the radio-frequency pulses, saturating nuclear spin system.

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

$$\frac{dQ_n}{dT} = C_n \frac{dT_n}{dt} = -\alpha \left(T_n - T_{el}\right), \tag{9}$$

$$\frac{dQ_{el}}{dt} = C_{el} \frac{dT_{el}}{dt} = -\beta \left(T_{el} - T_0\right) - \alpha'(T_{el} - T_n), \qquad \text{(case } a\text{)} \tag{10}$$

$$\frac{dQ_{el}}{dt} = C_{el} \frac{dT_{el}}{dt} = -\beta' \left(T_{el}^4 - T_0^4\right) - \alpha'(T_{el} - T_n), \qquad \text{(case } b\text{)} \tag{11}$$

Here α, α', β, β' 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 at liquid helium temperatures the heat capacity of the nuclear spin-system is very small in comparison with the conduction electron one we can neglect the second term in the equations (10), (11). Then, equations can be re-written in the more convenient form by introducing the inverse temperatures of systems – β_n, β_{el}, β_0 for nuclear spin system, conduction electron system and liquid helium correspondingly, and the dimensionless quantity m and n:

$$m = 1 - \beta_n/\beta_0 \quad \text{and} \quad n = 1 - \beta_{el}/\beta_0. \tag{12}$$

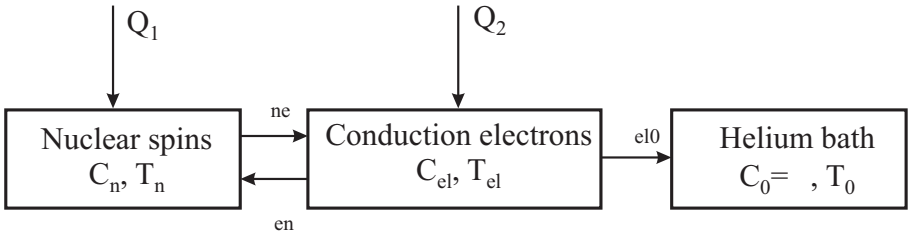

Fig. 9. The nuclear magnetization evolution at different initial saturation of ^{45}Sc NMR spectrum (see text for detailed explanations). For numerical calculation the nuclear relaxation time has been chosen equal to 600 ms

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

$$\frac{dm}{dt} = \frac{1}{\tau_{nel}}\frac{n-m}{1-n}, \qquad (13)$$

(case a)

$$\frac{dn}{dt} = -\frac{n}{\tau_{el0}};$$

$$\frac{dm}{dt} = \frac{1}{\tau_{nel}}\frac{n-m}{1-n}, \qquad (14)$$

(case b)

$$\frac{dn}{dt} = -\frac{1}{\tau'_{el0}}\frac{1-(1-n)^4}{1-n^2}.$$

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 Eqs. (13) or (14), and then take into account that nuclear magnetization M is proportional to the inverse nuclear spin temperature β_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 τ_{nel}, τ_{el0} and τ'_{el0} and initial deviations of the conduction electron temperature from the equilibrium value (the initial value of the parameter n). The results of numerical solutions for the time evolution of the quantity $m(t)$ are given on Figs. 10, 11. Calculations show that due to the heating of the conduction electron system by radio-frequency pulses the nuclear magnetic relaxation has essentially non-single exponential character.

Our measurements of longitudinal nuclear magnetic relaxation (see Fig. 5) are well described by usual exponential function and we are able to get the value of Korringa constant. But in some experimental situations especially at very low temperature and high rf-pulse power the overheating of conduction electron system can lead to non-exponential relaxation and difficulties in the getting of the correct value of Korringa constant.

Conclusions

We studied the nuclear magnetic relaxation in scandium metal in both powder and single crystal samples. Compared to previous NMR experiments on Sc, we paid attention on complete saturation of ^{45}Sc NMR spectrum in order to investigate the single

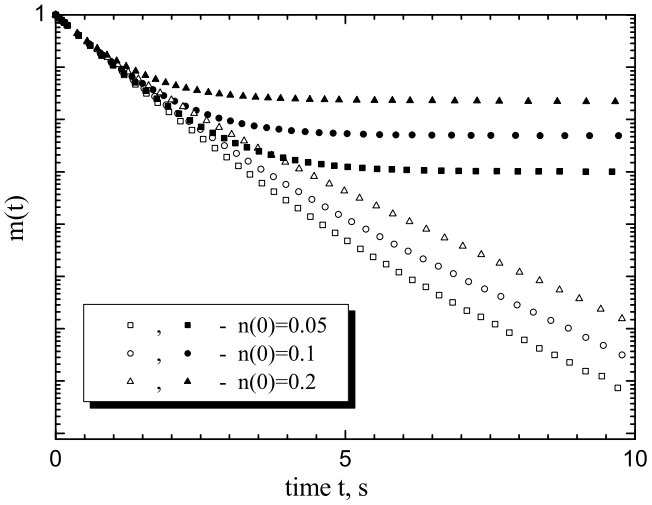

Fig. 10. The time evolutions of the quantity $m(t)$ obtained by numerical calculations of Eqs. (13) and (14). Open symbols correspond to the case of "usual" heat exchange (case *a*), whereas solid ones correspond to "Kapitza resistance" type of the heat exchange (case *b*). Kinetic parameters are the following: $\tau_{nel} = 1$ s, $\tau_{el0} = \tau'_{el0} = 2$ s. The initial conditions for the electron system are shown in the frame. The nuclear spin system is assumed to be complete saturated at initial time

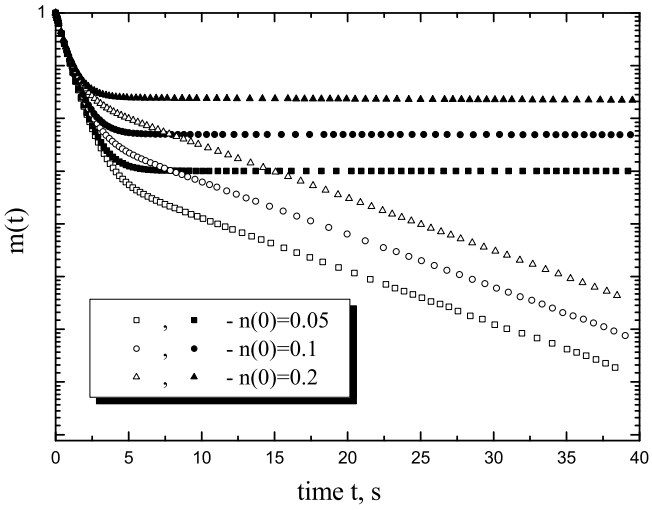

Fig. 11. The same as in Fig. 10. $\tau_{nel} = 1$ s, $\tau_{el0} = \tau'_{el0} = 10$ s

exponential decay of the longitudinal magnetization. The following conclusions can be emphasized from our investigations:

1) At liquid helium temperature Korringa constant has the magnetic field dependence. The origins of this dependence are the spin fluctuation effect and the impurity influence. Our theoretical analysis in the framework of SCR theory allows to consider the quenching of spin fluctuations in electron system at high magnetic field as most important reason for magnetic field dependence of Korringa constant. The further experimental investigations at more lower temperature can give the final answer.

2) There are at least two sources for non-exponential nuclear relaxation in scandium metal. They are the incomplete saturation of NMR spectrum and the overheating the conduction electron system by radiofrequency pulses. These factors have to be taken in account for correct interpretation of NMR data in scandium.

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Резюме

С. Абе, А.В. Егоров, М. Хондо, А.В. Клочков, И.Р. Мухамедшин, В.В. Налетов, Х. Сузуки, М.С. Тагиров, Д.А. Тюрский. Ядерная магнитная релаксация в металлическом скандии.

В работе исследована ядерная магнитная релаксация в металлическом скандии (монокристаллы и порошки) при низких температурах. Показано, что наблюдаемые температурная и магнитно-полевая зависимости постоянной Корринги могут быть объяснены за счет влияния спиновых флуктуаций $3d$ электронов. Наиболее вероятной причиной для уменьшения скорости ядерной релаксации в сильных магнитных полях является замораживание спиновых флуктуаций. Также проанализирована другая возможная причина – влияние магнитных примесей. Обсуждаются причины различий измеренных значений постоянной Корринги. Исследованы возможные источники неэкспоненциальной ядерной релаксации в металлическом скандии.

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