

**NUCLEAR MAGNETIC RELAXATION IN HYDROGEN-CONTAINING NIOBIUM
CAUSED BY MODULATION OF QUADRUPLE INTERACTION
BY MEANS OF TUNNEL TWO-LEVEL SYSTEMS**

L. L. Chotorlishvili¹

*Tbilisi State University, Department of Physics
Chavchavadze av. 3, Tbilisi 380028, Georgia*

Received 5 March 2001, in final form 6 November 2001, accepted 20 November 2001

Nuclear magnetic relaxation in niobium and hydrogen nuclei caused by modulation of quadruple interaction by means of a tunnel two-level system (TLS) has been investigated. It is shown that at low temperatures and high density of states, the relaxation caused by TLS dominates the relaxation of conduction electrons.

PACS: 76.60Es

In the recent years very active investigations of amorphous systems such as spin glasses, dielectric glasses, amorphous ferromagnetics, and hydrogen-containing metals modeled as tunnel two-level systems (TLS) have been carried out [1,2]. The concept of TLS model worked out for spin glasses has been after applied to hydrogen-containing metals, particularly to NbO_xH_y [3,4]. The works [5,6] deal with the influence of TLS upon the electronic spin-lattice, as well as upon the process of nuclear magnetic relaxation in various disordered samples. It was shown [5,6] that in many cases, the influence of TLS upon the processes of relaxation at low temperatures is of great importance, as with due account of this influence one can explain the experimentally observed temperature behavior of the spin-lattice relaxation time. A cross-relaxation of hydrogen and niobium nuclei in NbO_xH_y system was studied in [7]. In order to explain the anomalous behavior of longitudinal relaxation time T_1 of H nucleus the relaxation rate $1/T_1$ remains finite at $T < 10$ K for low frequencies of hydrogen nucleus $\omega_I \sim 5$ MHz and does not tend to zero in contrast to the Korringa mechanism [8]—the following mechanism has been proposed: the positional disorder of the H nuclei in the lattice causes a wide distribution of the electric field gradient on the Nb nucleus with the spin $J > 1$, leading to cross-relaxation at the coincidence of the Zeeman frequency of the H nucleus with the mixed Zeeman quadruple frequency of the Nb nucleus. Even if the mechanism explains the anomalous behavior of the relaxation time of the H nucleus, according to the authors, it is possible to use TLS model as a universal model for disordered systems at low temperatures. Essentially we suppose that H nuclei form TLS. The tunneling of hydrogen between two levels changes the gradient of electrical field on Nb nuclei and causes nuclear relaxation.

¹E-mail address: Lchotor@yahoo.com

Let us write the Hamiltonian of the interaction between Nb nuclei and TLS. The quadruple Hamiltonian for Nb nuclei is [9]:

$$\hat{H}_q = p_{11} \left[\left\{ (J^z)^2 - \frac{1}{3} J(J+1) \right\} + \frac{1}{3} \eta \left((J^+)^2 + (J^-)^2 \right) \right],$$

where $p_{11} = \frac{3}{2} p_{zz}$, $\eta = \frac{p_{xx} - p_{yy}}{p_{zz}}$, $p_{zz} = \frac{1}{2} \frac{eQq}{4J(2J-1)}$, Q is the quadruple moment and q is the electrical field gradient (see [10]).

Taking into account the fact that the nucleus can be in a nonsymmetric potential well, we can write

$$\hat{p}_{11} = \begin{pmatrix} p_{11}^1 & 0 \\ 0 & p_{11}^2 \end{pmatrix} = p_{11}^1 \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + p_{11}^2 \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \frac{p_{11}^1 + p_{11}^2}{2} \hat{I} + \frac{p_{11}^1 - p_{11}^2}{2} \sigma^z, \quad (1)$$

where p_{11}^1 and p_{11}^2 are the values corresponding to two different states of TLS, \hat{I} is the unit matrix, and σ^z is the Pauli matrix.

The second term in equation (1) describes the change of the electric field gradient [10] due to the jumps of TLS between two equilibrium positions [11]. An order-of-magnitude estimate of this term gives

$$(p_{11}^1 - p_{11}^2) d \sim \frac{d}{a} p_{11} d^z \sim 0.1 p_{11} d^z,$$

where d is the distance between the minima of TLS, d^z is the pseudo-spin operator and a is the separation between TLS and Nb nuclei.

Taking into account the above argument, we can write the Hamiltonian of the interaction between the Nb nuclei and the tunneling TLS as follows:

$$\hat{H}_{Jd} = \sum_{kn} A_{kn} \left[\left\{ (J_k^z)^2 - \frac{1}{3} J_k(J_k + 1) \right\} + \frac{1}{3} \eta \left((J_k^+)^2 + (J_k^-)^2 \right) \right] d_n^z,$$

where $A \approx \frac{d}{a} P_{11}$.

Let us use the unitary transformation operator

$$u = \exp(i\varphi d^y),$$

where $\tan \varphi = \Delta_0/\Delta$, Δ_0 is the tunneling parameter and Δ is the potential well asymmetry. Then, the Hamiltonian in the representation of TLS will be

$$\begin{aligned} \hat{H}_{Jd} &= \sum_{kn} A_{kn} \left[\left\{ (J_k^z)^2 - \frac{1}{3} J_k(J_k + 1) \right\} + \frac{1}{3} \eta \left((J_k^+)^2 + (J_k^-)^2 \right) \right] \times \\ &\times \left\{ \frac{\sqrt{\varepsilon_n^2 - \Delta_{0n}^2}}{\varepsilon_n} d_n^z + \frac{1}{2} \frac{\Delta_{0n}}{\varepsilon_n} (d_n^+ + d_n^-) \right\}, \end{aligned} \quad (2)$$

where $\varepsilon_n = \sqrt{\Delta_{0n}^2 + \Delta_n^2}$ is the TLS energy.

Thus, we can assume that the interaction (2) is responsible for relaxation. Let us write the total Hamiltonian of the system:

$$\begin{aligned} \hat{H} = & -\hbar\omega_I \sum_i I_i^z - \hbar\omega_J \sum_i J_i^z + \sum_n \varepsilon_n d_n^z + \sum_s \hbar\omega_s a_s^\dagger a_s + H_{IJ} + H_{Jd} + \\ & + \frac{8\pi}{3} \hbar^2 \gamma_J \gamma_S \sum_{ij} (S_i^+ J_j^- + S_i^- J_j^+) \delta(R_i - r_j) + H_{II} + H_{dd} + H_{JJ} + H_q, \end{aligned} \quad (3)$$

where H_q is the quadruple Hamiltonian for Nb nuclei, $\hbar\omega_s$ is the energy of conduction electrons, R_i is the radius-vector of conduction electrons, r_j is the radius-vector of Nb nuclei, $\hbar\omega_I$ is the Zeeman frequency of H nucleus, $\hbar\omega_J$ is the Zeeman frequency of Nb nucleus, I^z , J^z are the spin operators of H and Nb nuclei, d^z is the TLS pseudo-spin operator, γ_s and γ_j are the gyro-magnetic ratios for electrons and nuclei, a_s^\dagger , a_s are the second-quantizing operators of conduction electrons and S^\pm is the electron spin operator, which in the representation of the second-quantization has the following form [12]

$$\begin{aligned} S^-(R_i) &= \sum_{kk'} e^{i(k-k')R_i} u_k(R_i) u_{k'}^*(R_i) a_{k'\downarrow}^\dagger a_{k\uparrow} \\ S^+(R_i) &= \sum_{kk'} e^{i(k'-k)R_i} u_k^*(R_i) u_{k'}(R_i) a_{k\uparrow}^\dagger a_{k'\downarrow}, \end{aligned}$$

where the Bloch's zone number index is omitted, as the averaging is carried out only in the vicinity of the Fermi surface (see [13]). The Hamiltonians H_{IJ} , H_{dd} and H_{JJ} are the secular parts of the dipole-dipole interaction. Secular part does not affect the form of kinetic equations describing the relaxation process, however, it should be taken into account in the calculation of corresponding correlation functions. The interaction causing the cross-relaxation between Nb and H subsystems is given by

$$H_{IJ} = \sum_{ij} B_{ij}^{+-} (I_i^+ J_j^- + I_i^- J_j^+).$$

Let us consider the relaxation process as a thermodynamical process. For this assumption we use the method of non-equilibrium statistical operator (NEO) [14]. According to this method the time derivatives of the average values of the subsystem energy $\langle H_i \rangle_q = \text{Sp}(\rho_q H_i)$ (where $\rho_q = (\text{Sp} e^{-A})^{-1} e^{-A}$ is the local equilibrium distribution operator) are equal to the average of appropriate thermodynamical currents

$$\frac{d}{dt} \langle H_i \rangle_q = \langle k_i \rangle_{\text{NEO}},$$

where the averaging is done with respect to the density matrix

$$\rho_{\text{NEO}} = \text{Sp} \rho_q \left\{ 1 - (\beta_i - \beta) \int_0^1 d\lambda \int_{-\infty}^0 dt e^{\varepsilon t} e^{\lambda R} k_i(t) e^{-\lambda R} \right\}.$$

Here A and R are the well-known standard notations [14], β is the inverse temperature of the lattice, and β_i is the inverse temperature of i -th subsystem.

If we suppose that the subsystems of TLS and electrons are in thermal equilibrium with the lattice, after simple calculations (similar to those made by Zubarev [14]) we obtain the following set of equations in the high-temperature approximation for nuclear spins:

$$\begin{aligned}\frac{d\beta_J}{dt} &= -\frac{\beta_I - \beta}{T_{JI}} - \frac{\beta_J - \beta}{T_{JJ}} \\ \frac{d\beta_I}{dt} &= -\frac{\beta_J - \beta}{T_{IJ}} - \frac{\beta_I - \beta}{T_{II}},\end{aligned}\quad (4)$$

where

$$(T_{ij})^{-1} = -\frac{1}{\beta \frac{\partial}{\partial \beta} \langle H_i \rangle} \int_0^\beta d\lambda \int_{-\infty}^0 e^{\varepsilon t} \langle k_j(t - i\lambda) k_i \rangle dt, \quad (5)$$

β_I is the inverse temperature of the H subsystem, β_J is the inverse temperature of the Nb subsystem.

In expression (5), we replace d^z by the corresponding fluctuation $\delta d_n^z = d_n^z - \bar{d}_n^z$ and change the summation over indices by the integration with respect to TLS parameters (we use TLS parameters distribution function $p(\varepsilon \Delta_0)$ [1-2]). After simple calculations we obtain:

$$\begin{aligned}\frac{1}{T_{IJ}} &= \frac{4\gamma_J N_J J B^2}{\gamma_I N_I} G(\omega_I - \omega_J); & \frac{1}{T_{II}} &= 4B^2 J G(\omega_I - \omega_J) \\ \frac{1}{T_{JJ}} &= \frac{4\pi k_B T}{\hbar} \left(\frac{\Delta H}{H} \right)^2 \frac{\gamma_J^3}{\gamma_s^3} + \frac{B^2}{J} G(\omega_I - \omega_J) + \frac{4}{9} \frac{N_d}{N_J} A^2 \bar{p} + \\ &+ \frac{4}{9} \frac{N_d}{N_J} \frac{\tau}{1 + \omega_I^2 \tau^2} A^2 \bar{p} \ln \frac{\varepsilon_{\max} k_B T}{e \Delta_0 \hbar} \\ \frac{1}{T_{JI}} &= \frac{\gamma_I N_I}{\gamma_J N_J J} B^2 G(\omega_I - \omega_J),\end{aligned}\quad (6)$$

where γ and N are the corresponding gyro-magnetic ratios and concentrations, \bar{p} is the density of TLS states, T is the value of the temperature, k_B is the Boltzmann constant, J is the value of Nb spin, ε_{\max} is the maximum value of the TLS energy, τ is the correlation time of pseudo-spin correlation function $\langle d^z d^z(t) \rangle$ determined by the interaction between two-level systems, $\frac{\Delta H}{H}$ is the Nith factor [13] for Nb nucleus, $g(\omega)$ is the Fourier transform of the correlation function $g(t) = \frac{\langle J^+(t) J^- \rangle}{\langle J^+ J^- \rangle}$, and $G(\omega_I - \omega_J) = \int_0^\infty g_I(\omega) g_J(\omega + \omega_J - \omega_I) d\omega$.

The relatively small value of the correlation function

$$g'(t) = \frac{\langle (J^+(t))^2 (J^-(t))^2 (J^+)^2 (J^-)^2 \rangle}{\langle (J^+)^2 (J^-)^2 (J^+)^2 (J^-)^2 \rangle}$$

is neglected in expression (6).

As we have mentioned above, the main aim of the present paper is to demonstrate that the H relaxation rate is temperature independent because of the cross-relaxation between H and Nb nuclear spin subsystems. If Nb nuclei could quickly transfer the energy from the dipole system to TLS subsystem (TLS subsystem is considered to be in thermal equilibrium with the lattice) we can avoid the "bottle neck" problem. (It is easy to see that $C_J > C_I$, where $C_J = \partial\langle H_J \rangle / \partial T$, $C_I = \partial\langle H_I \rangle / \partial T$ are the heat capacities for Nb and H subsystems.) Owing to the temperature-independent part in the total relaxation time T_{JJ} , caused by the flip-flop process between Nb and TLS subsystems, this mechanism is more effective than Korringa mechanism at low temperature in case of high density of TLS states. In conclusion, we give some numerical estimates. Let us assume that

$$\frac{\Delta H}{H} \sim 0, 2; \quad \frac{\gamma_J^3}{\gamma_s^3} \sim 10^{-3}; \quad \frac{N_I}{N_J} \sim 10^{-2};$$

$$N_I \sim N_d; \quad J \sim 2; \quad A \sim 10^6 \text{ Hz}; \quad B \sim 10^4 \text{ Hz}; \quad T \sim 1 \text{ K}.$$

Then, we obtain:

$$\frac{1}{T_{IJ}} \sim 10^4 \text{ Hz}; \quad \frac{1}{T_{JI}} \sim 10^3 \text{ Hz}; \quad \frac{1}{T_{II}} \sim 10^3 \text{ Hz}; \quad \frac{1}{T_{JJ}} \sim 3 \cdot 10 \text{ Hz},$$

and for $\bar{p} \geq 10^{-12}$ the temperature-dependent part in the total relaxation time T_{JJ} , caused by TLS (mechanism of Klauder-Anderson) is more effective than Korringa mechanism:

$$\frac{\frac{4 N_d}{9 N_J} \frac{\tau}{1 + \omega_I^2 \tau^2} A^2 \bar{p} \ln \frac{\varepsilon_{\max}}{e \Delta_0} \frac{k_B T}{h}}{\frac{4 \pi k_B T}{\hbar} \left(\frac{\Delta H}{H} \right)^2 \frac{\gamma_J^3}{\gamma_s^3}} > 1.$$

Below the temperature $T < 0.01 \text{ K}$ becomes more important another flip-flop mechanism producing the temperature-independent part in T_{JJ} . Thus, the above estimates suggest that TLS can significantly affect the relaxation process at low temperatures.

References

- [1] P. W. Anderson: *Phil-Mag.* **25** (1972) 1
- [2] W. A. Phillips: *J. Low Temp. Phys.* **7** (1972) 351
- [3] H. Wipf: *Phys. Rev. Lett.* **52** (1984) 1308
- [4] H. Wipf: *Phys. Rev. Lett.* **46** (1981) 947
- [5] S. J. Szeftel, H. Alloul: *Phys. Rev. Lett.* **3** (1975) 657
- [6] T. L. Reinecke, K. L. Ngai: *Phys. Rev.* **B5** (1975) 122
- [7] L. R. Lichty: *Phys. Rev.* **B42** (1990) 7734
- [8] J. Korringa: *Physica* **16** (1950) 601
- [9] A. Abragam: *The principles of nuclear magnetism* (in Russian) IL, Moscow 1963
- [10] B. Bleaney: in *Hyperfine interactions*, Edited by A. J. Freeman, Academic press, New York-London 1967 p.11
- [11] L. L. Chotorlishvili: *Low Temp. Phys.* **24** (1998) 17
- [12] J. Winter: *Magnetic Resonance in Metals* (in Russian) Mir, Moscow 1975
- [13] C. P. Slichter: *Principles of magnetic resonance* (in Russian) Mir, Moscow 1981
- [14] D. N. Zubarev: *Non-equilibrium Statistical Thermodynamics* (in Russian) Nauka, Moscow 1971