Impurity Nuclear Spin–Lattice Relaxation Suppression and Charge Exchange of Chromium Ions in a γ-Irradiated Ruby Crystal

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The possibility of directly separating and measuring the impurity and lattice contributions to nuclear spin–lattice relaxation under the condition of a steady-state magnetic saturation is demonstrated in the particular case of ^{27}Al nuclei in a γ-irradiated ruby crystal. Contributions from trivalent and charge-exchanged chromium ions to impurity nuclear relaxation were separated. The number of charge-exchanged chromium ions was found. The spin relaxation time of Cr^{4+} centers was estimated. © 1998 Academic Press

INTRODUCTION

In real crystals, the spin–lattice relaxation time of quadrupole nuclei is known to be determined by two additive mechanisms: a lattice mechanism, which is responsible for nuclear relaxation in perfect samples, and an impurity one (*1*). When the concentration of paramagnetic impurities or other relevant point defects is enough low, impurity relaxation occurs via spin diffusion to these relaxation centers (*2–8*). Recent studies have shown that the concepts of spin–lattice relaxation driven by spin diffusion is rather general and turned out to be valid not only for insulating ionic crystals but also for amorphous solids (*9–11*), molecular crystals (*12, 13*), and ferroelectric crystals (*14*). Measurements of the impurity relaxation rate are of great importance for determining the concentration of impurities in various solids, including natural materials (see, for example, (*15*)). However, the efficiency of using NMR to this purpose is limited because the separation of lattice and impurity relaxation is often indefinite. Recently, a new method of separating the lattice and impurity contributions under the condition of a steady additional saturation of NMR line has been proposed in (*16, 17*). The method is based on the following thermodynamic ideas. Impurity relaxation via spin diffusion is effective when the local inverse spin temperature near defects, α_{loc}, is closer to the equilibrium value equal to the inverse lattice temperature, α_l, than the average value over the sample, $\langle \alpha \rangle$ (*5*). If the spin–lattice relaxation time is measured using the conventional saturation recovery procedure, impurity relaxation proceeds under the condition

$$\alpha_{loc} > \langle \alpha \rangle. \tag{1}$$

A rather strong additional magnetic (as well as acoustic or electric) steady saturation produces local heating of the nuclear spin system, corresponding to $\alpha_{loc} = 0$ while $\langle \alpha \rangle$ is equal to a steady-state value $\langle \alpha \rangle_{st} > 0$ (*18*). This means that the regions near impurities became warmer than the spin system in the main crystal volume and the inequality [1] is inverted. In this case the impurity relaxation should be turned off and the restoration of the magnetization in the sample should be caused by the lattice mechanism only. This makes it possible to measure the time T_1^{lat} corresponding to the lattice contribution to nuclear relaxation and then to calculate the impurity time T_1^{im} using the obvious relationship

$$(T_1^{\Sigma})^{-1} = (T_1^{lat})^{-1} + (T_1^{im})^{-1}, \tag{2}$$

where T_1^{Σ} is the total relaxation time due to both the lattice and the impurity mechanisms.

The method described above has been applied to NaI, NaCl, GaAs, and Al_2O_3 nominally pure and doped crystals (*16–20*). In the present paper we report results of using this method to study the spin–lattice relaxation of ^{27}Al nuclei in a γ-irradiated ruby crystal. It will be shown that the contributions from trivalent and charge-exchanged chromium ions to impurity relaxation of Al nuclei can be separated. This allowed us to find the number of charge-exchanged chromium ions and to estimate the spin relaxation time of Cr^{4+} centers.

EXPERIMENTAL

The Al_2O_3 single crystal under study was grown by the Verneuil technique. The concentration of chromium in the melt was 5×10^{-16} cm^{-3}. The sample was a cylinder with the axis perpendicular to the crystal c-axis. The measurements of the ^{27}Al spin–lattice relaxation time were carried out at 77 K with the NMR spectrometer in a constant field $B = 0.49$ T. Since ^{27}Al nuclei have the quadrupole moment ($I = \frac{5}{2}$), the energy levels of ^{27}Al in hexagonal Al_2O_3 crystals are not equidistant at arbitrary sample orientation in the magnetic field. As a result, the total relaxation process is a superposition of several exponential processes and the re-

laxation rate is different for different pairs of spin levels (*19, 21*). In this connection, we performed the measurements when the sample was oriented at the magic angle (*1*) and the energy levels were nearly equidistant. For this orientation, the magnetization recovery follows an exponential law with a single relaxation time (*19, 21*). The time τ of magnetization recovery was measured after a pulse saturation (*22*). The saturating steady magnetic field was applied at the Larmor frequency by means of an additional coil. Alternating current was produced in this coil by an additional generator. The steady saturation of the ^{27}Al spin system was characterized by the factor $Z_{st} = \langle \alpha \rangle_{st}/\alpha_1$ (*5*), which was measured as the ratio of the free-induction signal amplitudes after a $90°$ pulse with the additional magnetic field switched on and off. It should be noted that under the condition of a steady saturation, the spin–lattice relaxation time T_1 and the magnetization recovery time τ are related to one another by (*17, 23*)

$$T_1 = \tau/Z_{st}. \qquad [3]$$

The γ-irradiation was produced using a ^{60}Co source. The doses received were 4.5×10^7 and 10^8 rad. To return the sample to the initial state, it was heat treated at 1300 K for 48 h and then slowly cooled down to room temperature. As it has been shown in (*24*), this procedure is sufficient for removing paramagnetic centers induced by γ-irradiation.

RESULTS AND DISCUSSION

The dependence of the spin–lattice relaxation time calculated from measurements of τ using Eq. [3] on the saturation factor for the sample under study before irradiation is shown in Fig. 1. It can be seen that at low saturation levels (Z_{st} close to 1) the relaxation time is independent of Z_{st} and equal to 116 ± 2 s. This time can be obviously identified with T_1^{Σ}. At intermediate saturation, $0.3 < Z_{st} < 0.7$, the relaxation time increases monotonously with decreasing Z_{st} and again becomes constant at $Z_{st} < 0.3$. According to the aforesaid and results obtained in (*16–20*), one can suppose that the impurity relaxation turns off in the range of Z_{st} from 0.7 to 0.3. Thus, the relaxation time at strong saturation should be treated as T_1^{lat}. It follows from the measurements performed that $T_1^{lat} = 260 \pm 20$ s. This time agrees well with the spin–lattice relaxation time corresponding to the lattice contribution which has been found in (*19, 25*) for two different nominally pure Al_2O_3 crystals (270 and 260 s). The substitution of the values of T_1^{Σ} and T_1^{lat} into Eq. [2] makes it possible to calculate the impurity contribution $T_1^{im} = 210 \pm 30$ s. Generally, the impurity spin–lattice relaxation occurs due to all paramagnetic centers which are present in the crystal lattice. In the ruby sample under study, the impurity contribution can arise due to trivalent chromium ions and uncontrolled impurities of another kind. However,
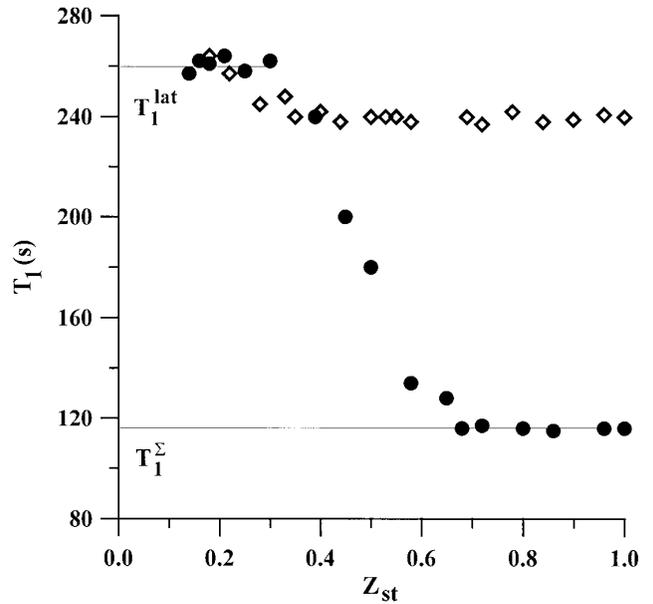

FIG. 1. The ^{27}Al spin–lattice relaxation time versus steady saturation for the chromium-doped (closed circles) and pure (open diamonds) Al_2O_3 crystals.

as shown in (*25*) for a chromium-free Al_2O_3 crystal, the contribution of uncontrolled impurities to the spin–lattice relaxation of ^{27}Al nuclei is very small; the corresponding time equals 3100 s. The dependence of T_1 in the pure Al_2O_3 crystal on the saturation factor Z_{st} is also shown in Fig. 1 for comparison. Thus, we can ascribe the found value of the impurity relaxation time in the ruby sample under study to trivalent chromium ions, entirely. The error followed from this assumption is within the limits of accuracy of evaluating the impurity relaxation time.

After γ-irradiation, the dependence of the spin–lattice relaxation time on the saturation factor changed significantly (Fig. 2). The value of the relaxation time at $Z_{st} = 1$ (without steady magnetic saturation) decreased for both doses of irradiation and an additional step appeared on the curves $T_1(Z_{st})$. However, as can be seen in Fig. 2, the lattice component of the relaxation time did not change and the complete suppression of the impurity contribution occurred at about the same saturation level ($Z_{st} \approx 0.3$) as before irradiation. It should be noted that the repeated heat treatment of the irradiated sample and irradiation with the same doses gave reproducible results. Within the framework of the model of the impurity relaxation suppression under strong magnetic saturation, the results obtained after γ-irradiation can be treated as follows. It has been shown in numerous papers (see, for example, (*26, 27*)) that γ-irradiation of ruby crystals leads to charge exchange of chromium ions and does not yield other electron centers. Some trivalent Cr^{3+} ions are converted to tetravalent Cr^{4+} and divalent Cr^{2+} ions. The concentrations of Cr^{4+} and Cr^{2+} ions are equal to each other because of the charge neutrality condi-
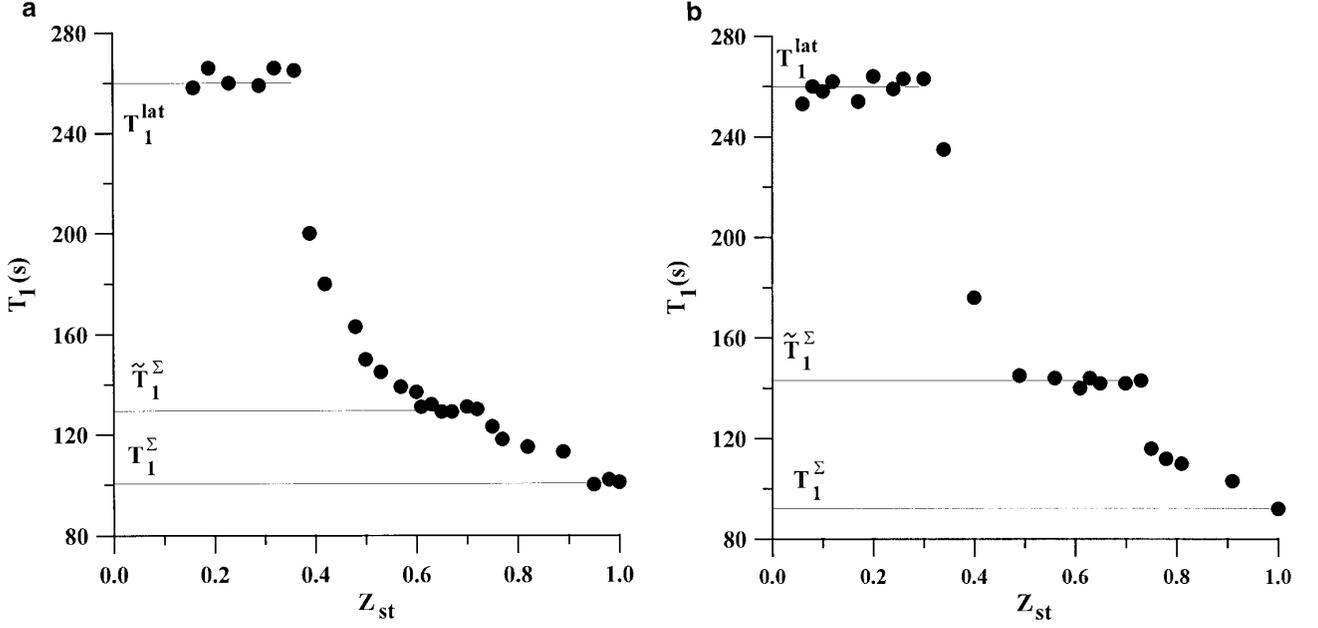
FIG. 2. The ^{27}Al spin–lattice relaxation time versus steady saturation for the chromium-doped Al_2O_3 crystal after γ-irradiation with doses of 4.5×10^7 rad (a) and 10^8 rad (b).

tion. It should be noted that in spite of a great number of studies devoted to the influence of γ-irradiation on ruby crystals, the concentration of charge-exchanged chromium ions was determined only very roughly. The appearance of tetravalent and divalent chromium ions affects the total relaxation rate of ^{27}Al nuclei. This accounts for the reduction of the spin–lattice relaxation time measured at $Z_{st} = 1$. The additional steps on the curves $T_1(Z_{st})$ in Fig. 2 correspond to incomplete suppression of the impurity relaxation. Since the behavior of T_1 at strong saturation almost did not change after irradiation (see Figs. 1 and 2), we can suppose that these steps show how the contribution of charge-exchanged chromium ions turns off. Denoting the relaxation time corresponding to the steps as $\tilde{T}_1^\Sigma$, we can find the time $T_{1,\gamma}^{Cr}$ of relaxation due to trivalent chromium ions after γ-irradiation:

$$T_{1,\gamma}^{Cr} = \{(\tilde{T}_1^\Sigma)^{-1} - (T_1^{lat})^{-1}\}^{-1}. \qquad [4]$$

The set of relaxation times obtained is listed in Table 1 for both

doses of irradiation together with the data for the sample before irradiation. The values of $T_{1,\gamma}^{Cr}$ enable us to estimate the concentration of trivalent chromium ions after irradiation. In fact, using the theory of impurity relaxation accompanied by spin diffusion (5) we can write for the relaxation via Cr^{3+} centers before irradiation

$$(T_1^{Cr})^{-1} = \frac{8\pi}{3} N C^{1/4} D^{3/4}, \qquad [5]$$

where N is the chromium concentration, C is the inverse time of nuclear relaxation via chromium at the unit distance from the impurity, and D is the spin-diffusion coefficient. Similarly, after irradiation

$$(T_{1,\gamma}^{Cr})^{-1} = \frac{8\pi}{3} N_\gamma C^{1/4} D^{3/4}, \qquad [6]$$

TABLE 1
Relaxation Parameters in the Ruby Crystal under Study before and after γ-Irradiation

Al_2O_3:Cr	T_1^Σ, s	T_1^{lat}, s	T_1^{im}, s	$\tilde{T}_1^\Sigma$, s	$T_{1,\gamma}^{Cr}$, s	N_γ/N	$\tilde{C}$, cm^6/s	$\tilde{N}_\gamma/N$
Before irradiation	116 ± 2	260 ± 20	210 ± 30					
After irradiation								
4.5×10^7 Rad	101.5 ± 0.9	260 ± 20		129 ± 4	260 ± 20	0.82	2.1×10^{-40}	0.09
10^8 Rad	92.6 ± 0.9	260 ± 20		142 ± 4	310 ± 30	0.68	2.6×10^{-40}	0.16

where N_γ is the concentration of trivalent chromium ions after irradiation. It follows from Eqs. [5] and [6] that

$$N_\gamma/N = T_1^{\text{Cr}}/T_{1,\gamma}^{\text{Cr}}. \qquad [7]$$

Using $T_1^{\text{Cr}} \cong T_1^{\text{im}}$ we can calculate the ratio N_γ/N. The values obtained are also listed in Table 1.

Let us now discuss the role of charge-exchanged chromium ions in the spin–lattice relaxation of ^{27}Al nuclei. According to (1), the parameter C in Eqs. [5] and [6] is written as

$$C \cong \frac{2}{5} \hbar^2 \gamma_S^2 \gamma_I^2 S(S+1) \frac{\tau_c}{1 + 4\pi^2 \nu_0^2 \tau_c^2}, \qquad [8]$$

where γ_S and γ_I are the gyromagnetic ratios of the chromium ion and the aluminum nucleus, respectively; S is the effective spin of the paramagnetic ion; τ_c is the spin relaxation time of the paramagnetic ion; and ν_0 is the nuclear Larmor frequency. A similar relationship is valid for tetravalent and divalent chromium ions. It follows from [8] that when the product $\nu_0\tau_c$ becomes much greater as well as much less than unity, the relaxation rate C decreases and the contribution of paramagnetic centers to nuclear relaxation is reduced. For tetravalent chromium ions in the ruby crystals at T = 77 K, τ_c should be around 10^{-9} s or shorter (28), as follows from the impossibility of observing the EPR signal at 77 K. Taking into account the value of $\nu_0 = 5.5$ MHz, we have $2\pi\nu_0\tau_c < 1$. For divalent chromium ions the spin relaxation time τ_c should be much shorter than that for tetravalent ions (29) because of stronger spin–lattice coupling. Then the contribution of divalent ions to nuclear relaxation can be neglected in comparison with that of tetravalent ions. Thus, the difference between the total impurity relaxation of ^{27}Al nuclei and relaxation due to trivalent chromium ions in the sample after irradiation should be entirely ascribed to tetravalent chromium ions. This makes it possible to calculate the concentration of tetravalent chromium ions, $\tilde{N}_\gamma$, and the value of the inverse time of nuclear relaxation at the unit distance from Cr^{4+} ions, $\tilde{C}$, relative to the corresponding values for trivalent chromium ions. Actually, the ^{27}Al spin–lattice relaxation time due to tetravalent chromium ions can be found from the following obvious relationship for the sample after irradiation:

$$\tilde{T}_{1,\gamma}^{\text{Cr}} = \{(T_1^\Sigma)^{-1} - (\tilde{T}_1^\Sigma)^{-1}\}^{-1}. \qquad [9]$$

The time $\tilde{T}_{1,\gamma}^{\text{Cr}}$ is described by Eq. [6] where N_γ and C are replaced with $\tilde{N}_\gamma$ and $\tilde{C}$, respectively. Then,

$$\left(\frac{\tilde{C}}{C}\right)^{1/4} = \frac{N_\gamma T_{1,\gamma}^{\text{Cr}}}{\tilde{N}_\gamma \tilde{T}_{1,\gamma}^{\text{Cr}}}, \qquad [10]$$

where $\tilde{N}_\gamma = (N - N_\gamma)/2$. The value of C at 77 K for trivalent

chromium ions in ruby crystals has been evaluated in (21) for the Larmor frequency 9.86 MHz. It is easy to recalculate it for our value of ν_0 using Eq. [8] and the estimate for τ_c from (30), $\tau_c = 4.4 \times 10^{-5}$ s: $C = 4.7 \times 10^{-43}$ cm^6/s. With this estimate for C we can calculate the absolute value of $\tilde{C}$. The values obtained for the two irradiation doses are listed in Table 1.

It is seen from Table 1 that for both doses of irradiation the calculated values of $\tilde{C}$ are in good agreement with each other. This speaks for the validity of the estimates performed. It follows also from Table 1 that the concentration of charge-exchanged chromium ions increases about linearly with increasing the irradiation dose. The value of $\tilde{C}$ obtained allows us to find the spin relaxation time of tetravalent chromium ions at 77 K using Eq. [8] and parameters of tetravalent chromium ions taken from (28): $\tilde{\tau}_c \approx 3 \times 10^{-8}$ s. This value agrees well with the fact that the EPR signal cannot be registered at the liquid nitrogen temperature because of very fast spin relaxation as noted in (28).

ACKNOWLEDGMENTS

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