

# Nuclear relaxation in SrF<sub>2</sub>

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The spin-lattice relaxation times of F<sup>19</sup> nuclei in an SrF<sub>2</sub> single crystal with Tb<sup>3+</sup> impurity ions are measured at temperatures between 0.3 and 77°K. It is shown that the theory of nuclear relaxation based on the concept of a Lorentz shape of the wings of the cross relaxation curve yields good agreement with the experiments in the low temperature region.

The investigation of nuclear spin-lattice relaxation (SLR) in diamagnetic crystals with paramagnetic impurities is of great interest. This pertains in particular to cases when appreciable polarization of the electron spins is attained. However, in the interpretation of the results of low-temperature measurements, there is frequently a discrepancy not only between the theoretical and experimental SLR times, but between the temperature dependences. In the present paper we report measurements of the SLR time of F<sup>19</sup> nuclei in single-crystal SrF<sub>2</sub> with Tb<sup>3+</sup> impurity ions in the temperature range 0.3–77°K. In the interpretation of the experimental results we have used the conclusions of the theory of SLR relaxation of nuclei via impurities, based on the assumption that the wings of the cross-relaxation curve have a Lorentz shape<sup>[1]</sup>.

The measurements were made with single-crystal SrF<sub>2</sub> grown by the Bridgman method in the Crystal-Growth Laboratory of the Kazan' State University. The impurity concentration in the blend was 0.5%. We used a pulsed coherent spectrometer at 13.4 MHz. The [111] axis of the crystal was oriented along the magnetic field H<sub>0</sub> by using the shape of the free-induction signal. The SLR relaxation time was determined from the spin-echo signal at different transmission frequencies. A metallic cryostat made it possible to operate in the temperature interval 0.3–77°K. Temperatures below 1.5°K were obtained by pumping off the vapor over liquid He<sup>3</sup> with a carbon pump cooled with liquid He<sup>4</sup> at 1.5°K, the coil with the sample being immersed directly in the liquid He<sup>3</sup>, thus preventing heating of the crystal by the radio-frequency pulses. The temperatures in the interval 0.3–1.5°K were measured by determining the vapor pressure over the liquid He<sup>3</sup>, and also with the aid of a carbon resistor.

The measurements were made in the temperature interval 1.5–77°K, both with a metallic cryostat and in a glass cryostat (with the sample heated).

The measurement results are shown in the figure. A broad maximum of the T<sub>1</sub>(T) curve is observed approximately at 60°K. Its presence is due to the fact that the condition ω<sub>0</sub>τ<sub>C</sub><sup>0</sup> = 1 is satisfied at this point, where τ<sub>C</sub><sup>0</sup> = 1.2 × 10<sup>-8</sup> sec is the electron-spin correlation time and ω<sub>0</sub> is the resonant frequency. The EPR and the relaxation of the Tb<sup>3+</sup> ions in SrF<sub>2</sub> were investigated in<sup>[2]</sup>. The observed temperature dependence of the SLR rate is described by the formula

$$T_{1s}^{-1} = K_0 \operatorname{cth} (4.71/T) + B_0 e^{-177/T}. \quad (1)$$

The measurements of our crystal at 4.3 and 1.7°K have made it possible to estimate K<sub>0</sub> (K<sub>0</sub> ≈ 10<sup>6</sup>). Thus, near the minimum the SLR time of the Tb<sup>3+</sup> do not serve as the correlation time, since it exceeds τ<sub>C</sub><sup>0</sup> by at least

two orders of magnitude. In addition, in this case there would be observed a narrow minimum, since the Orbach-Aminov processes with large Δ prevail here in the electron relaxation.

Thus, the correlation time is due to the spin-spin interactions between the ions. To calculate τ<sub>C</sub> we use the expression

$$\tau_c^{-1} = T_{2s}^{-1} + T_{1s}^{-1}, \quad (2)$$

where T<sub>2s</sub> increases with increasing temperature as a result of the growth of the polarization of the paramagnetic-ion spins. We note that for temperatures above 10°K, the polarization is inessential. Formula (11) of<sup>[3]</sup> shows that the value T<sub>2s</sub> = 1.2 × 10<sup>-8</sup> sec corresponds to a Tb<sup>3+</sup> impurity-ion concentration ~0.05%. Taking into account the features of the method of growing the crystal, and also the non-isomorphic character of the substitution, we can assume that the concentration of Tb<sup>3+</sup> ions in the crystal is smaller than in the original charge. Consequently, the value of the concentration of the impurity ions ~0.05%, obtained on the basis of the experimental determination of T<sub>2s</sub> is perfectly realistic.

A calculation of the spin-diffusion coefficient D, of the diffusion-barrier radius d, and of the "pseudopotential" radius b of the Tb<sup>3+</sup> ion, based on the known formulas<sup>[4]</sup> and performed for H<sub>0</sub> || [111], has shown that in the temperature region 0.3–10°K we have R > d > b, i.e., fast diffusion obtains. We note that the ratio d/b increases with decreasing temperature. Curve 1 of the figure represents the SLR relaxation times calculated by a formula from<sup>[4]</sup>

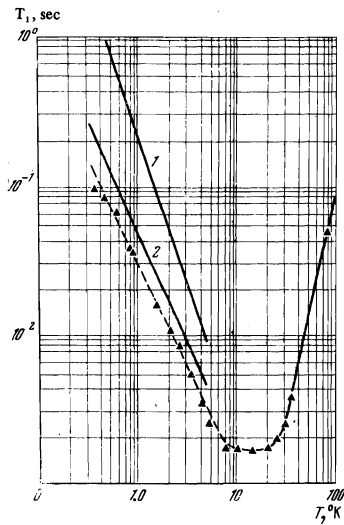
$$T_1 = R^3 d^3 / C, \quad (3)$$

where R is the radius of the sphere per ion. For temperatures lower than 4°K, when the condition ω<sub>0</sub>τ<sub>C</sub> > 1 is satisfied, we have in our case

$$C = 9 \cdot 10^{-18} \alpha / \tau_c, \quad \alpha = (\overline{\mu_z^2} - \mu_z^2) / \beta^2, \quad (4)$$

where μ<sub>z</sub> is the projection of the magnetic moment of the impurity and β is the Bohr magneton. We see that the calculated SLR times in the temperature interval 0.3–10°K are much higher than the observed ones, and that this discrepancy increases with decreasing temperature.

Good agreement between the theoretical and experimental values of the SLR time in the temperature range 0.3–10°K can be obtained from the theory based on the assumption that the cross-relaxation curve has Lorentz-shaped wings.<sup>[1]</sup> If the cross-relaxation curve is assumed to be Gaussian, then, as indicated in<sup>[4]</sup>, the spin diffusions at distances r < d from the magnetic ions can be neglected. It has been recently shown in a num-



ber of papers<sup>[5-7]</sup> that in both diluted and regular paramagnets, the cross-relaxation curve  $\varphi(\omega)$  has a Lorentz shape at  $\omega > \Delta\omega$ , where  $\Delta\omega$  is the homogeneous absorption line width. In this case, as shown by one of us<sup>[1]</sup>, the spin diffusion is effective at distances  $r < d$  and the approximation of the diffusion coefficient  $D$  by a rectangular function can lead to appreciable error. The expression obtained in this manner<sup>[1]</sup> for the SLR relaxation time in limiting cases yields

$$T_1 = 0,574R^3d^2b/C \quad \text{at } d \gg b, \quad (5)$$

$$T_1 = 1,6b^2R^2/C \quad \text{at } b \gg d. \quad (6)$$

The relaxation times calculated with the aid of (5) are shorter than the times given by (3) by a factor  $d/0.574b$ , which is quite significant at large ratios of  $d$  to  $b$ . Expression (6) coincides with the known result of<sup>[4]</sup>.

Curve 2 of the figure shows that calculation by means of formula (5) leads to an agreement with experiment in the low-temperature interval. We note that we have taken into account the polarization of the electron spins in the calculation of the SLR relaxation times. In the temperature interval  $T > 20^\circ\text{K}$  the role of  $\tau_c$  is assumed by  $T_{1s}$ . Calculation of  $b$  and  $d$  shows that  $b > d$  at  $T > 20^\circ\text{K}$ . We see from the figure that the experimental and theoretical values of the SLR time are in good agreement at  $T > 20^\circ\text{K}$ . This indicates that the relaxation is indeed determined by the  $\text{Tb}^{3+}$  ions, the concentration of which has been correctly determined.

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