

ANHARMONIC EFFECTS IN THE ELECTRON SPIN-LATTICE RELAXATION OF RADIATION DEFECTS IN POTASSIUM SELENATE AND ROCHELLE SALT SINGLE CRYSTALS

V.A. IVANSHIN, I.N. KURKIN

Kazan State University, Faculty of Physics
Lenina 18, 420008 Kazan, Russia

W. BRUNNER AND G. VÖLKEL

Universität Leipzig, Fachbereich Physik
Linnéstr. 5, O-7010 Leipzig, Germany

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An anharmonic character for the Raman processes of the electron spin-lattice relaxation of paramagnetic defect centres in γ -irradiated potassium selenate and Rochelle salt single crystals was observed at low temperatures.

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1. Introduction

The spin-lattice relaxation method is rather informative in investigations of peculiarities of vibrational spectra in crystals alongside with such methods as submillimeter spectroscopy, Raman spectroscopy and infrared light absorption [1]. We have measured the spin-lattice relaxation time T_1 of paramagnetic radicals $(\text{SeO}_3)^-$ being formed as a result of γ -irradiation in a potassium selenate (K_2SeO_4) single crystal which has been grown at the University of Saarbrücken (Germany). As it is known [2], the γ -irradiation of K_2SeO_4 leads to formation of few different radical types. We have studied the radical $(\text{SeO}_3)^-$ which causes the most intensive EPR line. The dose of irradiation was up to 5 Mrad. Measurements have been carried out in the temperature range between 4–180 K at the frequency of 9.4 GHz by means of the electron spin echo method at Leipzig University and using pulse saturation method at Kazan University.

The experimental data are compared with those we obtained recently [3] in Rochelle salt with the chemical composition $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$. The study

of the spin-lattice relaxation time T_1 of paramagnetic centres being formed as a result of X-irradiation has been carried out at two different frequencies 9.4 and 24 GHz in the temperature range between 1.5–300 K. The X-irradiation of Rochelle salt leads to the formation of three different radical types [4]. The OOC-C(OH)-CH(OH)-COO radical which gives the most intensive EPR line immediately after the irradiation has been studied. Rochelle salt single crystals were irradiated at room temperature using an X-ray tube working at 55 kV and 20 mA. The duration of irradiation was changed from 1 to 5 h resulting in an increase of the concentration of paramagnetic centres by a factor of three or four up to 10^{19} cm^{-3} . However, a concentration dependence of T_1 was not observed.

2. Experimental results

The results of the T_1 measurements are presented in Fig. 1 for Rochelle salt and in Fig. 2 for K_2SeO_4 . It has turned out that the temperature dependence of

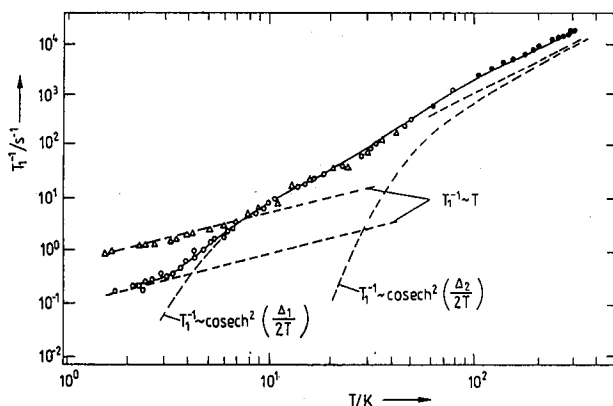


Fig. 1. Temperature dependence of the relaxation rate T_1^{-1} in X-irradiated Rochelle salt single crystals measured at 9.5 GHz (o) and 24 GHz (Δ); (\bullet) are taken from [5] (figure taken from Ref. [3]).

T_1^{-1} is analogous in both cases and can be described in the whole temperature range of measurements by

$$T_1^{-1} = AT + B_1 \operatorname{cosech}^2(\Delta_1/2T) + B_2 \operatorname{cosech}^2(\Delta_2/2T), \quad (1)$$

where the parameters A , B_1 , B_2 , Δ_1 , Δ_2 are given in Table I. The error of measurements leads to an error of the parameters Δ_1 and Δ_2 of about 10%.

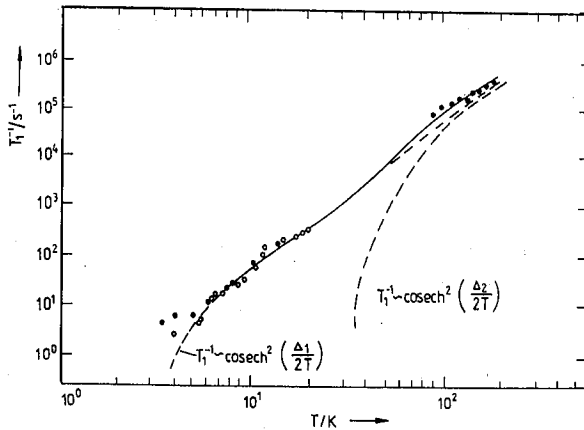


Fig. 2. Temperature dependence of the relaxation rate T_1^{-1} in γ -irradiated K_2SeO_4 single crystals measured at 9.4 GHz in Kazan (o) and Leipzig (\bullet).

TABLE I
Parameters of Eq. (1) obtained from a fit with the experimental data shown in Figs. 1 and 2.

Crystal	ν [GHz]	A [$s^{-1}K^{-1}$]	B_1 [s^{-1}]	B_2 [s^{-1}]	Δ_1 [K]	Δ_2 [K]
Rochelle salt	9.4	0.09	7.4	745	17.5	187
	24	0.5				
K_2SeO_4	9.4	—	185	1.2×10^5	27	206

3. Discussion

The first term in (1) corresponds to the direct relaxation process. The terms of type $\text{cosech}^2(\Delta/2T)$ are connected either with a two-phonon Raman process with an involvement of collective optical lattice vibrations with the energy $k\Delta$ [6, 7] or with a Raman process where a localized Einstein mode with the energy $k\Delta$ and acoustic lattice vibrations are involved [8].

Experimental optical investigations in Rochelle salt by means of the Raman spectroscopy [9] indicated the presence of optical lattice vibrations at the wave numbers 128 cm^{-1} and 135 cm^{-1} . Therefore, the lattice excitation with the wave number $\bar{\nu}_2 = \Delta_2 k/hc = (130 + 5) \text{ cm}^{-1}$ determined from the temperature dependence of T_1 may be attributed to this optical lattice vibration.

As light scattering experiments at optical phonons in K_2SeO_4 have revealed there exists indeed a mode at 140 cm^{-1} [10]. This is very close to the wave number $\bar{\nu}_2 = \Delta_2 k/hc = 143 \text{ cm}^{-1}$ corresponding to Δ_2 in potassium selenate.

We can conclude that the relaxation described by the third term in for-

mula (1) is determined by a Raman process with an involvement of optical lattice vibrations.

The lattice excitations with the wave number $\bar{\nu}_1 = \Delta_1 k/hc$, on the other hand, are not so easy to understand. The optical Raman spectra show no vibrations at the corresponding wave numbers 12 cm^{-1} in Rochelle salt and 18.6 cm^{-1} in K_2SeO_4 . The term $\text{cosech}^2(\Delta_1/2T)$ could be interpreted as caused by a localized Einstein mode at Δ_1 .

But there is also another interpretation for this term if we take into consideration what frequency the soft mode has in both crystals at very low temperatures. Below 20 K the soft mode in Rochelle salt and K_2SeO_4 takes the value $\bar{\nu}_{\text{SM}} = 22 \text{ cm}^{-1}$ [11] and 36 cm^{-1} [12], respectively. In both cases it becomes apparent that $\bar{\nu}_1 \simeq \bar{\nu}_{\text{SM}}/2$. It has been shown theoretically [13] that in a special case of a Raman relaxation process where strongly anharmonic quasi-localized vibrations with frequency ω_{local} are involved the subharmonic $\omega_{\text{local}}/2$ appears in the argument of the Raman term. From this point of view the term Δ_1 may be related with an anharmonic quasi-localized vibration at the frozen-in soft-mode frequency.

4. Conclusion

According to this interpretation the anharmonic character of the Raman spin-lattice relaxation in irradiated K_2SeO_4 and Rochelle salt single crystals points to a distortion of the frozen-in soft mode at temperatures below 20 K due to the studied paramagnetic defects.

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