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Solid State Communications, Vol. 26, pp. 853–855. 0038–1098/78/0615–0853 $02.00/0
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ELECTRON SPIN–LATTICE RELAXATION IN Mn^{2+}-DOPED FERROELECTRIC TSCC

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(*Received* 21 *January* 1978 *by P.G. de Gennes*)

The spin–lattice relaxation of ferroelectric TSCC : Mn^{2+} has been investigated by means of the electron spin echo method in the range between 4.2 and 160 K. In the vicinity of the phase transition an anomalous increase of T_1 has been detected deviating from the spin–lattice relaxation in the remaining temperature range.

1. INTRODUCTION

A SERIES of studies has been published concerning EPR line width anomalies observed in systems which undergo structural phase transitions of second order. As shown in a previous paper [1] also a temperature anomaly of the spin–lattice relaxation has been observed in such systems. However, in contrast to the transverse relaxation rate which determines the EPR line width and increases drastically near the ferroelectric phase transition, the spin–lattice relaxation rate decreases. This effect stated by the authors in X-irradiated triglycine sulfate has been detected in Mn^{2+}-doped trissarcosine calcium chloride (TSCC) too.

TSCC ($(CH_3NH_2^+CH_2COO^-)_3 \cdot CaCl_2$) is a uniaxial ferroelectric of the order–disorder type with a phase transition of second order at 127 K [2]. EPR investigations revealed the Mn^{2+} ions are incorporated at Ca^{2+} sites within an almost trigonal-deformed oxygen octahedron [3]. Each sarcosine molecule is linked with two Ca^{2+} ions thus forming an endless chain of octahedrons along [100]. The EPR line splitting observed in the ferroelectric region could be explained by tilting and deformation of the zero-field splitting tensor due to the spontaneous polarization. It is also the reason for the influence to be expected of the polarization fluctuations near the ferroelectric phase transition both on the transverse and the longitudinal EPR relaxation rate of the Mn^{2+} probe.

2. EXPERIMENTAL

TSCC : Mn^{2+} single crystals were grown by slow evaporation from an aqueous solution of sarcosine and $CaCl_2$ in the stoichiometric ratio on addition of a few mole percent $MnCl_2 \cdot 4H_2O$. From measurements of the EPR line intensity we know that the Mn^{2+} ion concentration rises from 3×10^{18} cm^{-3} to 2×10^{19} cm^{-3} if the $MnCl_2$ concentration in the solution is raised from 0.05 to 5 mole %.

Measurements of the dielectric permittivity of TSCC crystals containing Mn^{2+} ions with a concentration of 10^{19} cm^{-3} have been carried out and compared with the results obtained from pure crystals. They revealed a difference in the phase transition temperatures of less than 0.06 K.

All electron spin-echo (ESE) measurements have been performed in the X-band. A $\pi/2$-pulse sequence was used for determining the transverse relaxation time T_2 together with a $\pi-\pi/2-\pi$-pulse sequence and a change in the repetition rate of the $\pi/2-\pi$-sequence, respectively, to measure the spin-lattice relaxation time T_1. For the temperature range higher than 77 K the sample was cooled by means of a stabilized nitrogen gas flow with an accuracy better than ± 0.05 K. Between 4.2 and 30 K a helium cryostat and a microwave cavity with inner heating have been used.

The ESE measurements have been carried out with the static magnetic field H_0 applied parallel to the crystallographic [100] direction where the four chemically equivalent Mn^{2+} sites become magnetically equivalent.

3. EXPERIMENTAL RESULTS

The phase memory time T_M measured by a $\pi/2-\pi$-pulse sequence at 77 K, which in the present case should be equal to the transverse relaxation time T_2, decreases with rising Mn^{2+} concentration,

$$T_M^{-1} = T_{M_0}^{-1} + \alpha C \qquad (1)$$