Comparison of ^{35}Cl NQR Spectra between the Mixed Crystals $K_2Sn_{1-x}Re_xCl_6$ and the Al^{3+} Doped Crystals K_2SnCl_6:Al^{3+} *,+

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^{35}Cl Nuclear Quadrupole Resonance (NQR) has provided a valuable tool for investigating the local structure in mixed crystals $K_2Sn_{1-x}Re_xCl_6$ and Al^{3+} doped crystals K_2SnCl_6:Al^{3+}. The measured NQR line shapes and relaxation times of both kinds of impurity containing crystals in the cubic phase of the host K_2SnCl_6 show markedly different impurity effects; static impurity effects in $K_2Sn_{1-x}Re_xCl_6$ and dynamic effects in K_2SnCl_6:Al^{3+}. The ^{35}Cl NQR spectra of K_2SnCl_6:Al^{3+} near the transition temperature (T_c) indicate the presence of pretransition of the local structure in the high temperature cubic phase.

I. Introduction

Potassium hexachlorostannate (K_2SnCl_6) belongs to the family of antifluorites A_2BX_6, where A, B, and X represent respectively alkali, transition metal ions and halogens (Fig. 1a). Many of these compounds exhibit magnetic and displacive structural phase transitions. The structural phase transitions in A_2BX_6 are driven by the condensation of the rotary lattice mode, which changes to the thermally activated rotation of the SnX_6^{2-} octahedra, the hindered rotation, at high temperatures. Thus the hindered rotation seems to be also of particular importance for the crystal instabilities and consequently to the structural transitions in A_2BX_6.

K_2SnCl_6 undergoes two structural phase transitions at 262 and 256 K on decrease of the temperature with change of the crystal symmetry from face centered cubic at high temperatures to monoclinic at low temperatures through an orthorhombic intermediate phase (Figure 1b).

In order to obtain a comprehensive description of the dynamical instabilities of the lattice, optic, and X-ray or neutron scattering as well as nuclear resonance investigation of the A_2BX_6 mixed crystals, where both starting materials belong to the same antifluorite family, have been intensively carried out [1 - 5].

The concentration dependence of the transition temperature $T_c(x)$ is well described by the relation

$$T_c(x) = T_c(0)\frac{1 + ax}{1 + bx}, \qquad (1)$$

where a and b are fitting parameters based on a mean field description of random systems [4]. This relation has been confirmed by the NQR study on mixed A_2BX_6 crystals (Figure 2).

On the other hand, for Al^{3+} doped crystals, where the parent crystals are not isostructural, a smooth fit of impurities is hardly expected due to the topological and chemical differences of the starting materials. In this case, the substitution of impurities would produce various kinds of defects in the crystal. Therefore the NQR spectra of these kinds of impurity doped crystals would reflect the secondary impurity effect related to the static and dynamic properties of the impurity induced lattice defects.

In this contribution, the data on the variation of the ^{35}Cl NQR spectra of the K_2SnCl_6 matrix in mixed crystals $K_2Sn_{1-x}Re_xCl_6$ with Re^{4+} concentration are presented in the first part of Sect. IV, and the effect

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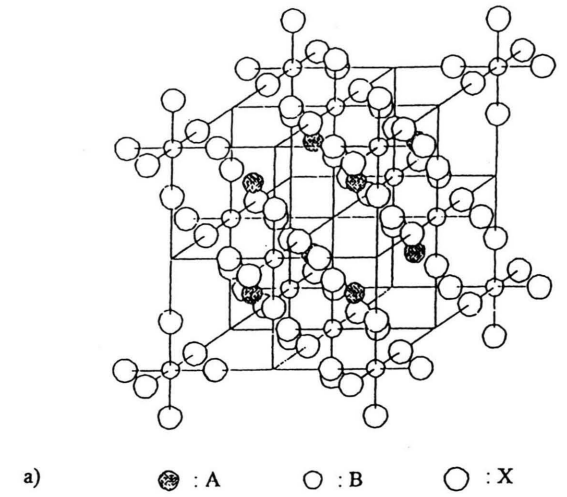

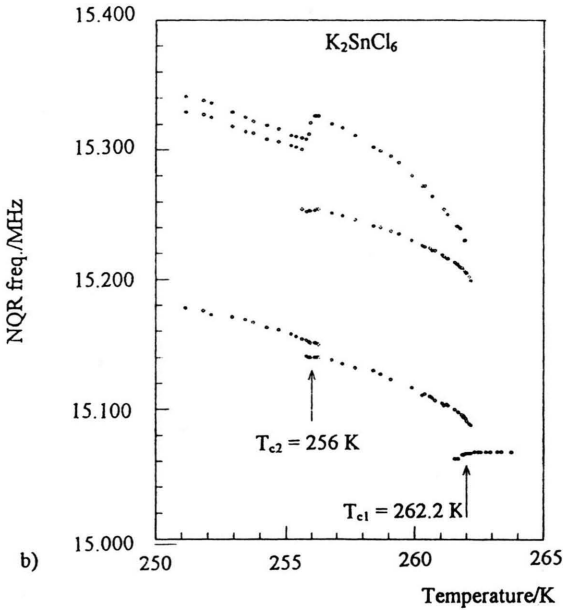

Fig. 1. a) Cubic antifluorite structure A_2BX_6; b) ^{35}Cl NQR frequency of K_2SnCl_6 as a function of temperature near the transition temperatures T_{c1} and T_{c2}.

of the substitution of Al^{3+} ions on the ^{35}Cl NQR of K_2SnCl_6 in the Al^{3+} doped K_2SnCl_6, K_2SnCl_6:Al^{3+} in the second part of Sect. IV. The ^{35}Cl NQR spectra of $K_2Sn_{1-x}Re_xCl_6$ and K_2SnCl_6:Al^{3+} differ much. The NQR spectra of $K_2Sn_{1-x}Re_xCl_6$ reveal predominantly quasi-static impurity effects, while those of K_2SnCl_6:Al^{3+} indicate in many respects dynamic disorder, especially near T_c.

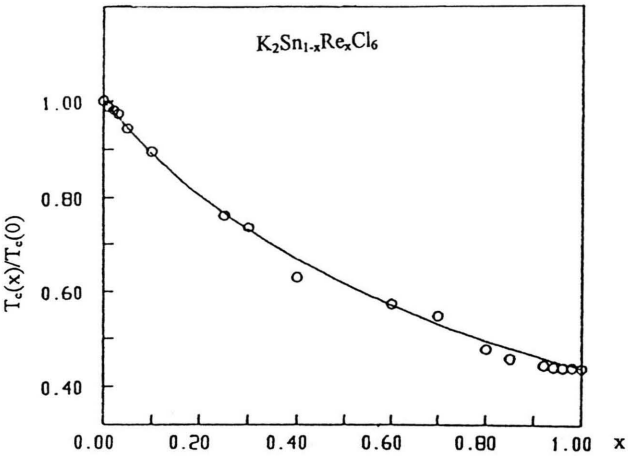

Fig. 2. Phase transition temperature of the mixed crystal system $K_2Sn_{1-x}Re_xCl_6$ as a function of impurity concentration. The solid line is the fit of (1) to the data.

II. ^{35}Cl NQR in the Cubic Phase of K_2SnCl_6

The theoretical background of NQR can be found in [6]. The NQR hamiltonian is given by

$$\hat{H}_q = \hat{I} \cdot \overleftrightarrow{Q} \cdot \hat{I}, \tag{2}$$

where $\hat{I}$ is the nuclear spin operator and $\overleftrightarrow{Q}$ the quadrupolar tensor that contains the electric field gradient (efg) at the nuclear site and the quadrupole moment of the nucleus.

In the principal axes system, the quadrupole hamiltonian can be represented by two independent parameters, the maximum component of the efg $V_{zz} = eq$, where e is the electronic charge and η the asymmetry parameter, which is the measure of the deviation of the efg from the cylindrical symmetry along the z axis. In the case of ^{35}Cl, $I = {}^3/_2$, the separation of the energy levels, which is doubly degenerate, yields a resonance frequency

$$\nu_q = \frac{e^2qQ}{2h}\sqrt{1+\frac{\eta^2}{3}}. \tag{3}$$

In the high temperature cubic phase of K_2SnCl_6, all chlorine nuclear sites are equivalent, and $\eta = 0$ due to the cubic site symmetry, yielding one resonance frequency

$$\nu_q = \frac{e^2qQ}{2h}. \tag{4}$$

III. Sample Preparation and Experiment

K_2SnCl_6 and K_2ReCl_6 were made by the methods described in [4]. Powdered samples of the mixed hexachlorometallates $K_2Sn_{1-x}Re_xCl_6$ were obtained by rapidly recrystallizing a highly saturated solution of K_2SnCl_6 and potassium hexachlororhennate (K_2ReCl_6) for $0 \leq x \leq 1$. Doping of Al^{3+} in K_2SnCl_6 was achieved by evaporating a solution of K_2SnCl_6 and aluminum chloride ($AlCl_3$). From the results of atomic and spectroscopic analyses, the actual Al^{3+} concentration, x, in the Al^{3+} doped K_2SnCl_6 crystals, K_2SnCl_6:Al^{3+}, is supposed to be much smaller than the nominal concentration over the whole range of x investigated, while in the mixed system the nominal concentration is generally in good agreement with the actual concentration. The homogeneity of the samples was checked by Raman scattering and X-ray diffraction analysis.

The NQR experiments were carried out with a Bruker pulsed spectrometer using a pulse width of around 7 μs for the 90° pulse at the spectrometer frequency of 15 MHz. The temperature was regulated with a temperature controller (Cryogenic S 3010) by controlling the flow of liquid nitrogen drops and the heat current.

IV. ^{35}Cl NQR Results and Discussion

1. Mixed Crystals $K_2Sn_{1-x}Re_xCl_6$

NQR Results at Temperatures Far Above the Transition Temperature

Besides the static line broadening, one important impurity (Re^{4+}) effect on the resonance line of the K_2SnCl_6 matrix is the appearance of the satellite lines in addition to the original resonance line (Figure 3). Two important features of the line spectra containing the original and satellite lines are as follows

a) The frequencies of the satellite lines are higher than that of the original line, and they are located regularly from the original resonance line with an equidistant sequence of OL - 1SL - 2SL - 3SL - 4SL, where OL denotes the original line and nSL the n-th satellite line.

b) The intensities of the original line and the satellite lines change systematically such that the relative intensity of the n-th line is described by the binomial function

$$I_n(x) = \frac{4!}{(4-n)!n!}(1-x)^{4-n}x^n, \qquad (5)$$

where $I_0(x)$ and $I_n(x)$ are the intensity of the original line and the n-th satellite line, respectively.

Closer examination of the local charge distribution around the Cl site, which possesses fourfold symmetry about the Sn-Cl bonding axis, suggests that the satellite lines are produced if any of the 4 next nearest Sn^{4+} sites, from the position of the Cl nucleus under consideration, are occupied by Re^{4+} impurities. Therefore the intensity of the original and the satellite lines would be directly dependent on the probability for these lattice sites to be occupied by Re^{4+}. Figure 3 shows that the intensities predicted by (5) are in good agreement with the observed results. Here the frequency distance between neighbouring lines corresponds to the change in the value of q caused by each replacement of Sn^{4+} by Re^{4+}.

NQR Spectra Near the Structural Phase Transitions

With decreasing temperature both starting compounds K_2SnCl_6 and K_2ReCl_6 undergo the first structural phase transitions at 262 K and 111 K, respectively. A simple way to monitor the transition in K_2SnCl_6 is observing the cubic line, which disappears suddenly at the transition temperarure. Below T_c (= T_{c1} in Fig. 1b) three lines appear in K_2SnCl_6, corresponding to the orthorhombic structure. The general features of phase transitions in mixed crystals are as follows;

a) A monotonous shift of the transition temperature as a function of x between two transition temperatures of parent crystals $T_c(0)$ for K_2SnCl_6 and $T_c(1)$ for K_2ReCl_6 as predicted by (1) (Fig. 2) and

b) Rounding of the sharp anomalies at T_c (Fig. 4b) and a strongly nonexponential character in the spin-lattice relaxation near T_c (Figure 5a).

Smearing of the phase transition and the nonexponential relaxation can be easily understood in terms of the spatially macroscopic inhomogeneity in the impurity concentration in mixed crystals by considering (1) and the fact that, in most cases, the relaxation changes rapidly near the transition point. The nearly exponential decay of the spin magnetization recovery at temperatures far above T_c becomes increasingly nonexponential as the temperature approaches T_c, due to the inhomogeneous distribution of the impurities. Near T_c, the recovery curve is described actually

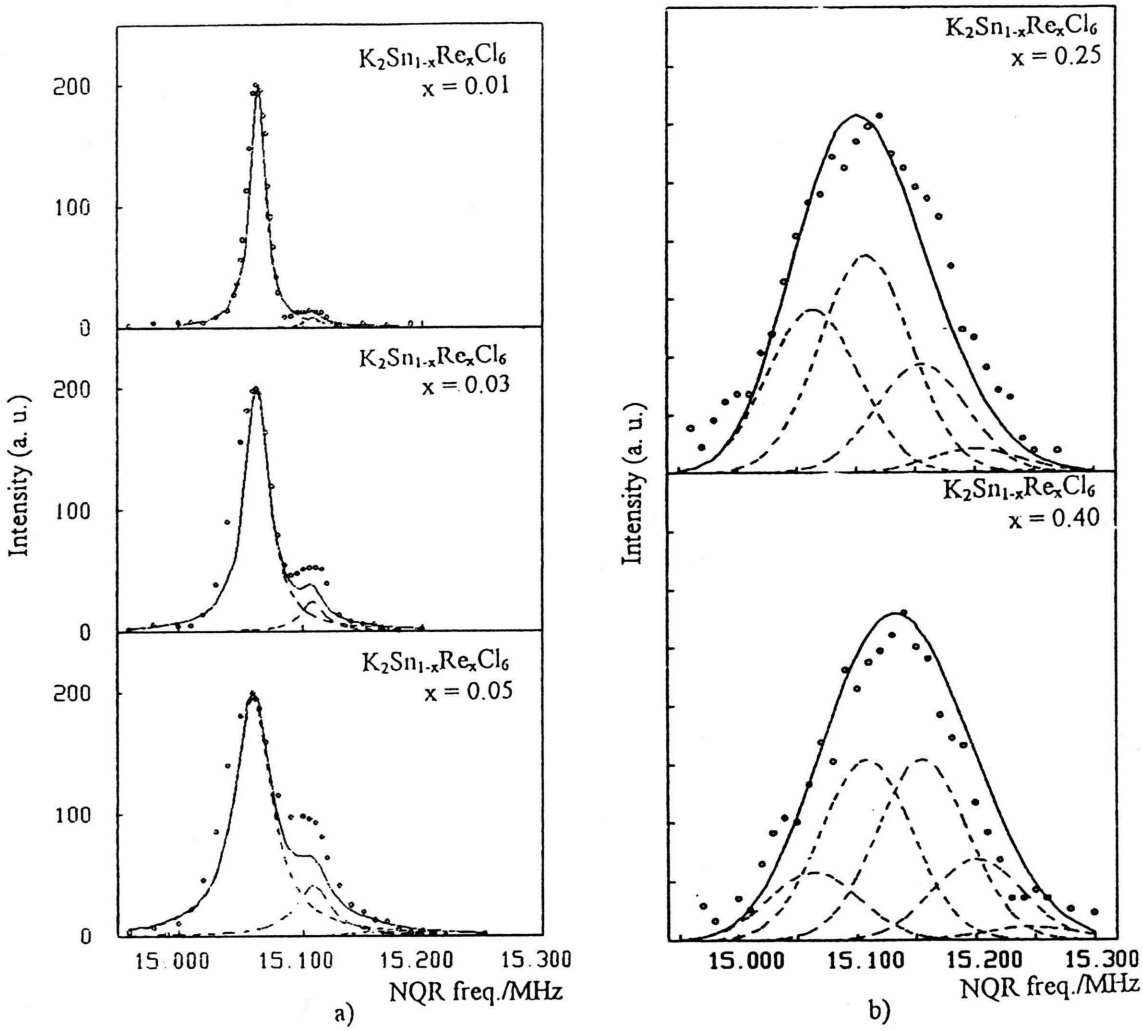

Fig. 3. ^{35}Cl NQR line spectra of the K_2SnCl_6 structure in $K_2Sn_{1-x}Re_xCl_6$ for a) small $x(\leq 0.05)$ and b) large x $(0.25 \leq x \leq 0.40)$. The dashed lines denote the individual line (original and satellite lines) intensities, and the solid line the sum of all line intensities.

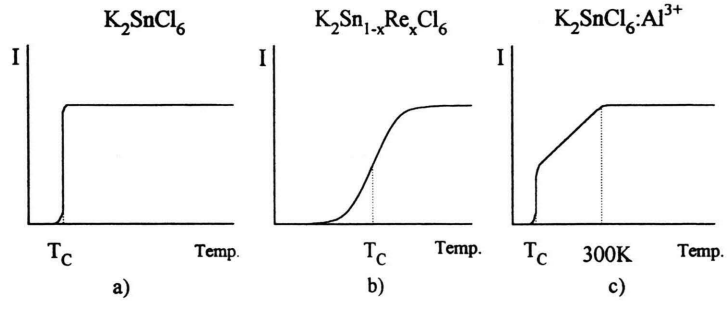

Fig. 4. Schematic representation of the cubic line intensity around the transition temperature for a) K_2SnCl_6 (T_c = 262 K), b) $K_2Sn_{1-x}Re_xCl_6$, and c) K_2SnCl_6:Al^{3+} (T_c = 262 K).

by a large number of exponential functions, each of which is represented by its own spin-lattice time T_1 (Figure 5a). The strongly nonexponential character of the recovery curve near T_c is again a sign of the macroscopic spatial inhomogeneities in the impurity concentration in mixed crystals.

Both phenomena, the appearence of the satellite lines and the strongly nonexponential spin lattice

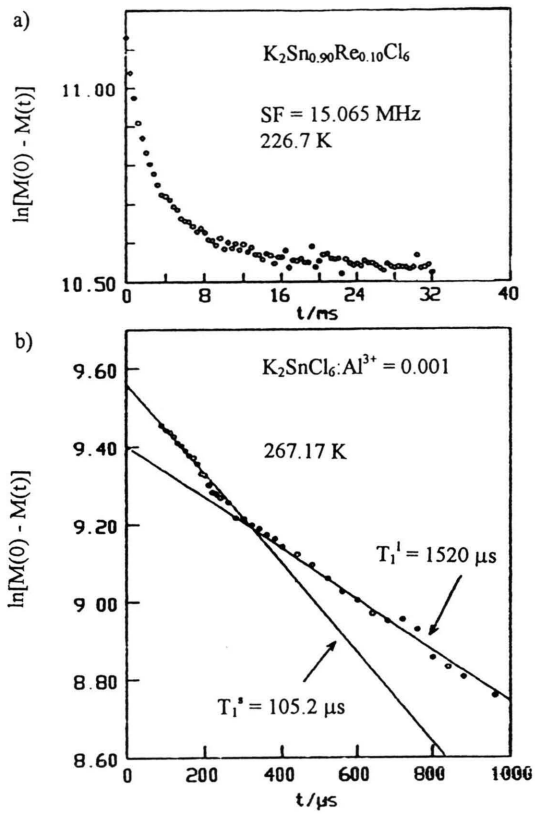

Fig. 5. Typical recovery of the chlorine nuclear magnetization in a) $K_2Sn_{1-x}Re_xCl_6$, and b) K_2SnCl_6:Al^{3+}.

relaxation near T_c indicate that in the mixed crystals the dominant impurity effect on the ^{35}Cl NQR is a static effect caused by the static random distribution of Re^{4+} ions at the Sn^{4+} sites and the spatially inhomogeneous distribution of the Re^{4+} concentration.

2. *K_2SnCl_6:Al^{3+}*

The NQR spectra of K_2SnCl_6:Al^{3+} contrast sharply to those of the mixed crystals $K_2Sn_{1-x}Re_xCl_6$ due to the crystallographic and chemical differences between the starting materials.

NQR Frequency and Line Width

Figure 6 displays the line width of K_2SnCl_6:Al^{3+} as a function of the logarithmic impurity concentration (solid line). The concentration dependence of the line width of the mixed system is also shown for comparison (dashed line).

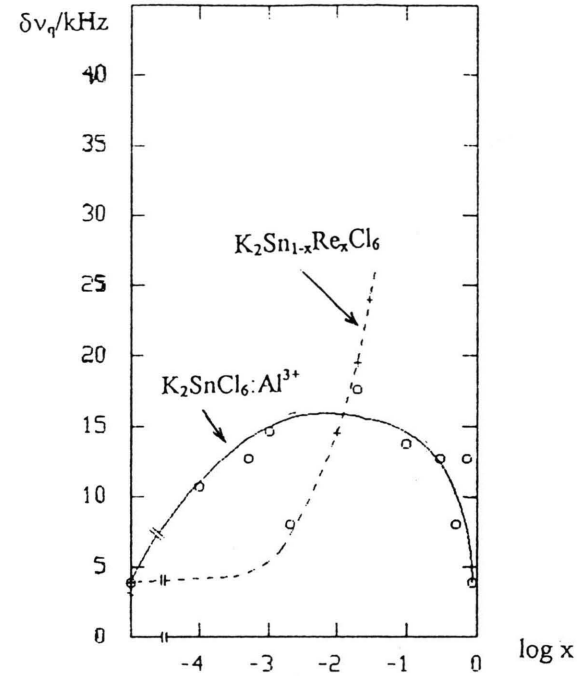

Fig. 6. Plot of the line width $\delta\nu_q$ against log x. The solid line and dashed line are guides to the eye. o : K_2SnCl_6:Al^{3+}; + : mixed crystals.

The line width of the doped crystal over the impurity content investigated ($0 \leq x \leq 0.85$: nominal concentration) is restricted at room temperature to the values of 3.9 ~ 17 kHz, whereas in the mixed system the maximum value of the line width amounts to ~ 100 kHz (Figure 3b). The dependence on the impurity concentration of the line width is peculiar compared to that of $K_2Sn_{1-x}Re_xCl_6$. The line width increases at first with increasing Al^{3+} concentration till it approaches a maximum value of ~ 17 kHz at about x = 0.02. Above this concentration, the line width decreases again with further increase of x and reaches finally the value at x = 0.85, which is essentially the same as that of the pure K_2SnCl_6. This line width behaviour differs much from that of the mixed crystal system $K_2Sn_{1-x}Re_xCl_6$, where the line width seems to be relatively insensitive against impurity below x = 0.01, and above this concentration it diverges abruptly with increasing x (Fig. 6: +, dashed line).

The fact that the line width increases by no more than ~ 17 kHz with further increase in impurity content implies that there is a line narrowing because of the fast motion of lattice defects. The concentration dependence of the line width indicates that, at small concentration, immobile defects are produced

predominantly and these defects contribute to the line broadening resulting in a rapid increase in line width with increasing concentration. With further increase in concentration the fraction producing mobile lattice defects becomes more and more predominant. Because of their fast motion, the line broadening is limited to the maximum value of 17 kHz, and it decreases even again with further increase in concentration x due to the increase in the density of the mobile lattice defects approaching again the value comparable to the line width of the pure K_2SnCl_6.

Temperature Dependence of Relaxation

High temperatures in the cubic phase can be divided into two regions at around 300 K according to the temperature behaviour of the relaxation times. Above 300 K, the temperature dependence of the relaxation times T_1 and T_2 is essentially the same as that of the pure K_2SnCl_6. The main relaxation mechanism here is, for both T_1 and T_2, the thermally activated hindered rotation of the $SnCl_6^{2-}$ octahedra, whose relaxation times have an exponential temperature dependence.

Below 300 K, both the magnetization recovery for T_1 and the spin echo decay for T_2 become nonexponential. In fact, they can be represented exactly by two exponential functions corresponding to two kinds of relaxation times, the shorter (s) and the longer (l) time T_1^s, T_2^s and T_1^l, T_2^2, respectively (Figure 5b). This double exponential character becomes more and more pronounced as the temperature approaches T_c from above (Figure 7). Though the presentation of the data on the spin echo decay for T_2 are here omitted, they show also clearly the double exponential character, whose temperature dependence is exactly the same as that for T_1. By comparing with the relaxation time in the pure K_2SnCl_6, the longer relaxation time can be immediately identified to be of the same kind as that occurring in the pure K_2SnCl_6.

Double exponential magnetization recovery and spin echo decay curves corresponding to the longer and shorter relaxation times imply that the crystal consists of two sublattices, which are subject to the shorter and longer relaxation. The fact that the relaxations are represented here only by two exponential function, while the relaxation in the mixed crystals $K_2Sn_{1-x}Re_xCl_6$ near T_c contains a large number of exponential functions, suggests that the substitution of impurities here induces not a spatial inhomogeneity

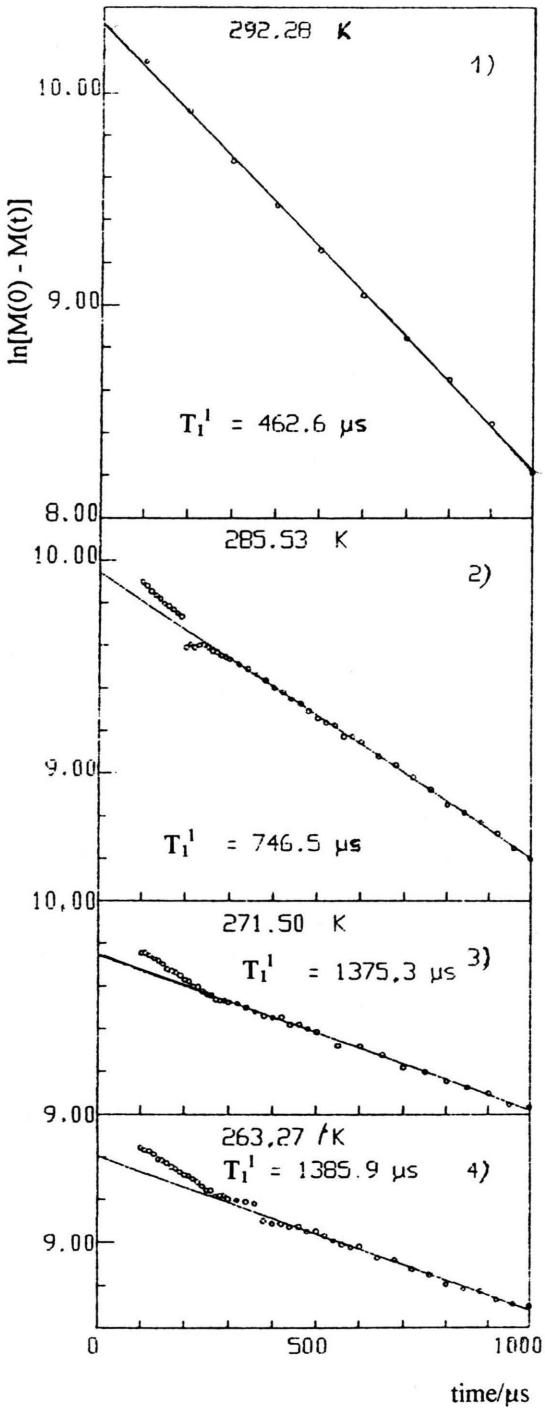

Fig. 7. A semi-logarithmic plot of the recovery of the ^{35}Cl nuclear magnetization in K_2SnCl_6:Al^{3+}, x = 0.0005 in the cubic phase at temperatures near T_c.

but a dynamic inhomogeneity, i. e., two sets of sublattices which are different in lattice dynamics.

Temperature Behaviour of T_1^s and T_2^s at $T_c \leq T \leq 300$ K

The distinctive features of both short relaxation times T_1^s and T_2^s are as follows.

a) Both T_1^s and T_2^s values are roughly the same if they are measured at the same temperature.

b) The fraction of the shorter relaxation increases at the expense of that of the longer relaxation as the temperature approaches T_c (Figure 7).

The same values of T_1^s and T_2^s imply that the relaxation is nonresonant, i. e., it is not induced by the lattice vibrations but by the strong fluctuation of local fields.

On the other hand, the cubic line intensity shows an unusual temperature behaviour near T_c (Figure 4c); With decreasing temperature the line intensity begins to decrease at 300 K, just at which the shorter relaxation begins to appear. The line intensity decreases further till the temperature becomes $T_c = 262$ K, at which the rest of the line intensity drops sharply. This critical behaviour of the line intensity apparently differs from the rounding of the critical anomaly in mixed crystals caused by the static inhomogeneity in the crystal (Fig. 4b). Comparing with the temperature dependence of the shorter relaxation, it can be easily noticed that the temperature behaviour of the shorter relaxation is responsible for the unusual critical behaviour of the cubic line intensity near T_c.

All these features in K_2SnCl_6:Al^{3+} indicate the presence of a pretransition of local structures in the high temperature cubic phase, that execute a slow structural fluctuation between the high temperature cubic phase and the low temperature phase.

A similar phenomenon was previously observed in the ^{35}Cl NQR invetigation of K_2OsCl_6 by [7]. However the double exponential character was observed only for the spin-lattice relaxation corresponding to T_1^s and T_1^l in the powder sample. In their study an explanation for the presence of $T_1{}^s$ was given in terms of the formation of dynamic clusters fluctuating between the high and low temperature phase.

Summary

The mixed crystals $K_2Sn_{1-x}Re_xCl_6$ and the Al^{3+} doped K_2SnCl_6 show quite different impurity effects on NQR spectra.

In $K_2Sn_{1-x}Re_xCl_6$, the presence of satellite lines at room temperature and the strongly nonexponential recovery curve of the chlorine nuclear magnetization are attributed to the random distribution of Re^{4+} ions at the Sn^{4+} sites and the spatial inhomogeneity in the Re^{4+} concentration.

In K_2SnCl_6:Al^{3+}, the double exponential character of the recovery curve of the nuclear magnetization for T_1 and the decay curve of the spin echo for T_2 below 300 K indicate that the lattice consists of two sublattices, which are subjected to different lattice dynamics corresponding to the shorter relaxation times T_1^s, T_2^s and the longer relaxation times T_1^l, T_2^l.

The critical behaviour of the shorter relaxation times T_1^s, T_2^s and their nonresonant character indicate the presence of pretransition local structures in the cubic phase, that fluctuate between the high temperature cubic phase and the low temperature phase.

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