

# Impurity Effects on the Local Structure in the Mixed Hexachlorometallate ( $A_2BCl_6$ : $A = K, Rb, B = Sn, Re, \text{ and } Pb$ ) Studied by the Chlorine NQR

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Chlorine NQR was studied for the isostructural hexachlorometallate mixed system. The study shows that Isomorphic hexachlorometallate solid solutions exhibit often impurity induced local structural order because of their relatively clear local site symmetry. This is manifested in the formation of a few satellite lines near the original resonance line and results from the random distribution of impurities on the lattice sites of the corresponding counterpart ions. Using the point charge model and a simple binomial function for the occupation probability of the guest ions on the host lattice sites, the position and the line intensity could be determined, the results of which are in good agreement with the NQR-observation. The temperature region of lattice dynamics in the crystal seems to shift in proportion to the impurity content. This fact explains the gradual change of the transition temperature in the mixed crystal between two starting materials.

**Key words:** NQR; Hexahalmetallates; Phase Transition; Mixed Crystals.

## 1. Introduction

$A_2BCl_6$  belongs to the family of antifluorite crystals with a chemical formula  $A_2BX_6$ . A stands for the alkali metal ion, M the transition metal ion in 3d-, 4d-, and 5d-series, and X the halogen. The high temperature crystal structure of  $A_2BX_6$  is face centered cubic with a space group  $O_h^5 - Fm3m$ . Among hexachlorometallates it is relatively easy to produce mixed crystals because of their structural and chemical similarities. In the crystal the  $BX_6$ -octahedra fill the  $A^+$ -cage alternatively (Figure 1).

These crystals are characterized by their richness of the lattice dynamics and the magnetic properties, of which the latter is determined by the electron configuration of the transition metal ion,  $B^{4+}$ . A unique feature at the high temperature lattice dynamics in  $A_2BX_6$  is the sudden and infrequent reorientational motion of the  $BX_6$ -octahedra, that changes into the rotary lattice mode with decreasing temperature. This motion is inherently associated with the crystal instability. Thus these crystal reveal a variety of structural and magnetic phase transitions as

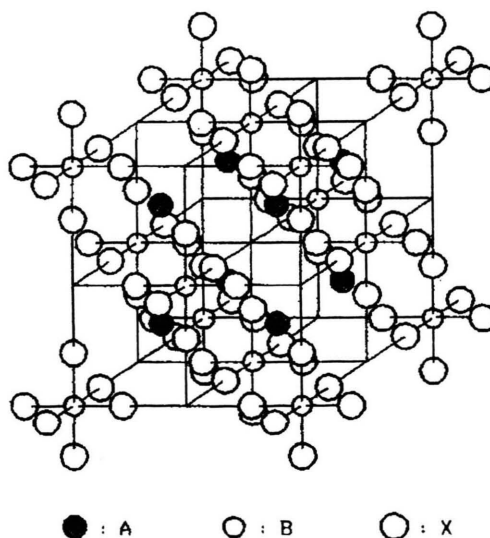


Fig. 1. Cubic antifluorite structure  $A_2BX_6$ .

expected from the lattice dynamical and magnetical properties.

This contribution concerns the Cl NQR study on a few kinds of mixed hexachlorometallates and the

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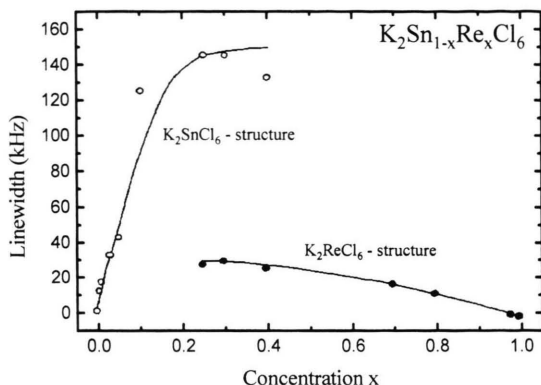


Fig. 2. Linewidth as a function of impurity concentration in  $K_2Sn_{1-x}Re_xCl_6$ .

nature of the impurity induced local disorder at room temperature. Among them,  $K_2(Sn-Re)Cl_6$  is particularly considered. Both crystals  $K_2SnCl_6$  and  $K_2ReCl_6$  were the prototype for the investigation of lattice dynamics and structural phase transitions which are now well understood [1 - 3].

Both  $K_2SnCl_6$  and  $K_2ReCl_6$  undergo successively two rotative structural phase transitions within a few degrees of temperature gap, where collective and permanent rotation of octahedra occurs. Thus this type of transition is inherently triggered by the rotational motion of octahedra yielding a correlation between the activation energy of the octahedral rotation and the transition temperature: Crystals with a high transition temperature tend to have a low activation energy.

On the other hand, the magnetic properties of  $K_2SnCl_6$  and  $K_2ReCl_6$  are quite different. This is originated from the difference in the electron configuration of the central transition metal ion  $Sn^{4+}$  and  $Re^{4+}$  with zero and non-zero total net spins respectively. Thus  $K_2ReCl_6$  is paramagnetic at room temperature and the magnetic transferred hyperfine interaction caused by the fast motion of the electron spin affects the NQR spectra in addition to the hindered rotation of the  $ReCl_6$ -octahedra at high temperatures. Compared with that,  $K_2SnCl_6$  is diamagnetic having an advantage for studying the lattice dynamics and related structural phase transitions, since the NQR spectra is not masked by the influence of the magnetic interaction, which is insensitive to the temperature change, as in  $K_2ReCl_6$ .

One of the main object in the study of the mixed crystal has been the investigation of the influence of the impurity on the phase transition mechanism [1, 2],

which is explained in the context of the virtual crystal approximation [4] and the Landau theory [5]. This model yields a transition temperature of the mixed crystal  $T_c(x)$  as function of impurity concentration

$$T_c(x) = T_c(0) \frac{1 + \alpha x}{1 + \beta x} \quad (1)$$

where  $\alpha$  and  $\beta$  are fitting parameters based on a mean field description of random systems. Equation (1) connects smoothly both transition temperature of the starting materials.

## 2. Results and Discussion

### 2.1. The Cl NQR Spectra

Above room temperature both crystals  $K_2SnCl_6$  and  $K_2ReCl_6$  yield a single resonance line corresponding to the cubic structure. The linewidth in  $K_2SnCl_6$  amounts to about 4 kHz which is usual for the solids having the nuclear magnetic dipole-dipole interaction. On the other hand, in  $K_2ReCl_6$ , the linewidth amounts to about 3/4 times of that of  $K_2SnCl_6$ . The partial line narrowing in  $K_2ReCl_6$  is attributed to the fast fluctuation of the electron spins in  $Re^{4+}$  that allows the electron-nuclear exchange interaction.

The NQR spectra in the whole range of impurity concentration  $x$  at room temperature show the resonance line of the  $K_2SnCl_6$ -structure or the  $K_2ReCl_6$ -structure. In mixed crystals with large concentration of impurities ( $x = 0.3 - 0.7$ ) both structures are observed. For the small concentration of impurity, namely, either  $x \approx 0$  or  $x \approx 1$ , at the both sides of the pure crystals, a single resonance line appears corresponding to the  $K_2SnCl_6$ - or  $K_2ReCl_6$ -structure. With increasing impurity concentration, i. e., the concentration of  $Re^{4+}$  for  $K_2SnCl_6$ - and the  $Sn^{4+}$  for  $K_2ReCl_6$ -structure, the linewidths of the  $K_2SnCl_6$ -structure and  $K_2ReCl_6$ -structure increase. However, the linewidth of the  $K_2SnCl_6$ -structure grows more rapidly than that of the  $K_2ReCl_6$ -structure (Figure 2). The position of the resonance lines remains for both structures unchanged.

One large difference in the NQR spectra for the  $K_2SnCl_6$ -structure and  $K_2ReCl_6$ -structure is that  $K_2SnCl_6$ -structure shows four satellite lines in addition to the original resonance line, whereas the  $K_2ReCl_6$ -structure lacks the corresponding feature. The fraction of the intensity of the satellite lines to

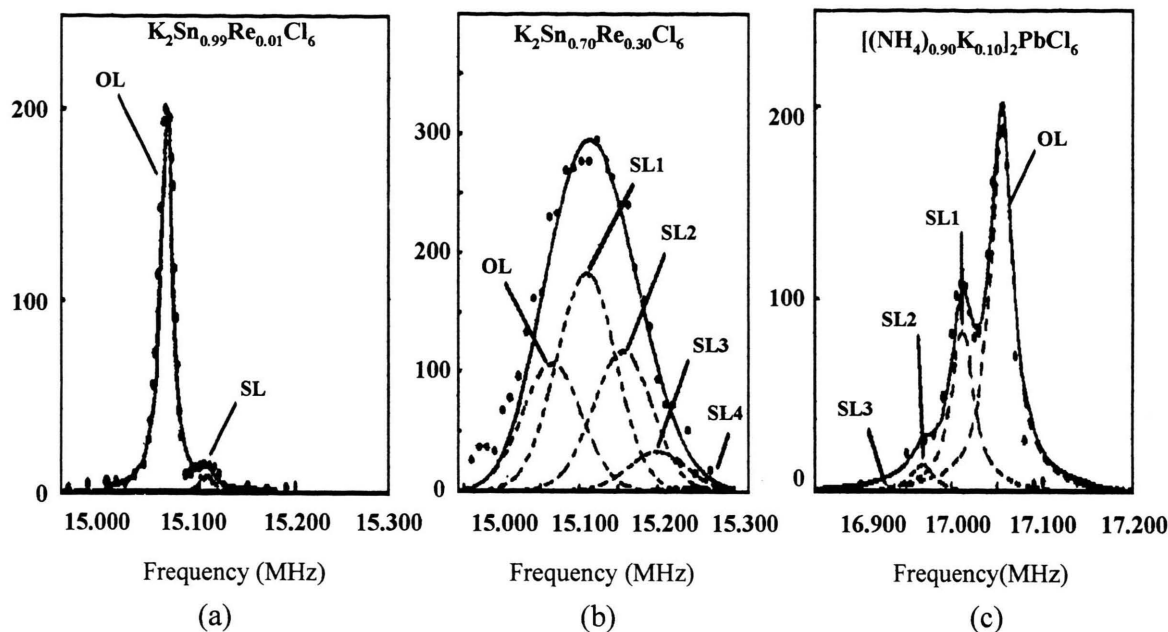


Fig. 3. NQR spectra of a few mixed crystals at room temperature. The dashed lines are fits to equ. (2), and the solid line is the superposition of them.

the original line increases in proportion to the  $\text{Re}^{4+}$ -concentration, they are all located above the original resonance line and they are all, including the original line, equidistant. These features of the satellite lines are common for all isostructurally mixed crystals irrespective of the kinds of component (Figure 3). The characteristics of the satellite lines is attributed to the random distribution of the  $\text{Re}^{4+}$ -ions at the  $\text{Sn}^{4+}$ -sites resulting in the formation of the local structural order. The total number of the satellite lines has a relation with the four-fold local site symmetry whose axis gets through the  $\text{Sn-Cl}$  bonding axis.

The relative intensity of the  $n$ -th line, counted from the original resonance line, is then proportional to the occupation probability for the  $\text{Re}^{4+}$ -ions at the  $\text{Sn}$ -site that forms four-fold symmetry and described by a simple binomial function

$$l_n = l_0 \frac{4!}{(4-n)!n!} (1-x)^{4-n} x^n \quad (2)$$

where  $l_0(x)$  and  $l_n(x)$  are the intensity of the original and the  $n$ -th satellite line respectively. The prediction of equation (2) is on the whole in accordance with the data (Figure 3).

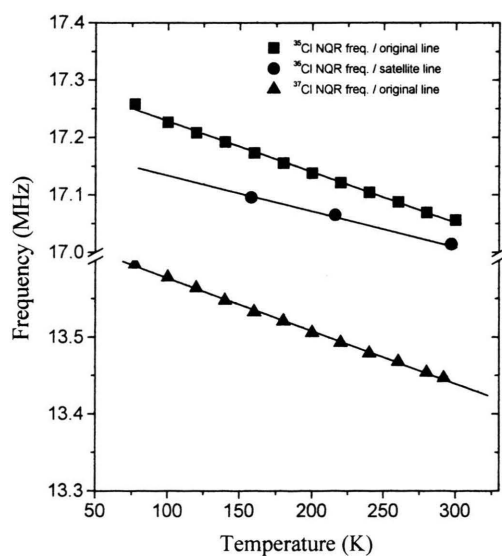


Fig. 4. Temperature dependence of the Cl NQR frequency in  $[(\text{NH}_4)_{0.90}\text{K}_{0.10}]_2\text{PbCl}_6$ .

The random distribution of the static  $\text{Re}^{4+}$  impurities at the  $\text{Sn}^{4+}$ -lattice sites is evidenced by the observation of the temperature behaviour of the satellite lines with respect to the original resonance line and

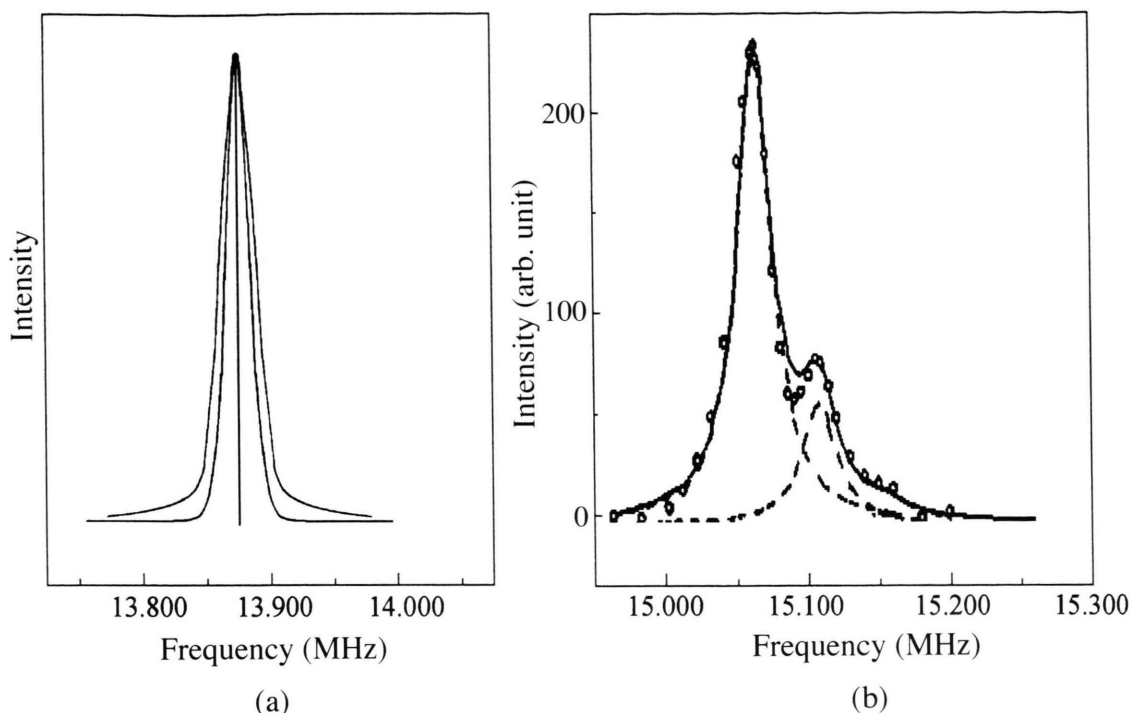


Fig. 5. NQR spectra at room temperature (a) the  $\text{K}_2\text{ReCl}_6$  structure (b) the  $\text{K}_2\text{Sn}_{1-x}\text{Re}_x\text{Cl}_6$  structure. The straight line in (a) indicates the position of the resonance line  $\text{K}_2\text{ReCl}_6$ .

that of the isotope nuclei  $^{37}\text{Cl}$ . For the two isotope nuclei  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , the phonon distribution around each isotope should be the same because of the same environment which predicts the same temperature dependence for  $^{37}\text{Cl}$ - and  $^{35}\text{Cl}$  NQR. However in the case of the satellite lines which are produced by the presence of impurities near the resonant nuclei, the phonon distribution is different and the temperature dependence of the NQR frequency for satellite lines should also change, if the masses are different for host and impurity ions, as the data for  $[(\text{NH}_4)_{1-x}\text{K}_x]_2\text{PbCl}_6$  show (Figure 4). In this mixed crystal  $\text{NH}_4$  and  $\text{K}$  have apparently different masses 18 and 39 in the atomic mass unit respectively.

The frequencies of the satellite lines of the  $\text{K}_2\text{SnCl}_6$ -structure in  $\text{K}_2(\text{Sn-Re})\text{Cl}_6$  which are all higher than that of the original line are, to a certain extent, reminiscent of the change of the resonance frequency at the transition temperature  $T = T_{c1}$  where the single cubic line is splitted into three lines corresponding to the orthorhombic structure. Their frequencies are all higher than that of the cubic line and

the increase in frequency at  $T = T_{c1}$  is proportional to the square of the rotation angle [6]. Comparing the frequency change at the transition to the resonance frequency of the satellite lines suggests that the replacement of the  $\text{Sn}^{4+}$  by  $\text{Re}^{4+}$  causes a similar effect on the local field at the nuclear site as the rotation of the octahedron, of which the resonant nucleus in question is a part.

On the other hand, the NQR spectra of the  $\text{K}_2\text{ReCl}_6$ -structure show no additional lines and the width of the original line increases relatively slowly with increasing  $\text{Sn}^{4+}$ -concentration (Fig. 2 and 5). This may be attributed to the difference of the electronic configuration of the  $\text{Re}^{4+}$ -ions from that of the  $\text{Sn}^{4+}$ -ions. Because of the presence of the hyperfine interaction the resonant nuclei in the  $\text{K}_2\text{ReCl}_6$  structure experience a fluctuation of the local field, the characteristic frequency of which is much larger than the resonance frequency, which is also responsible for the partial line narrowing. The formation of the local structural order is also wiped out by the fast fluctuation of the local field.

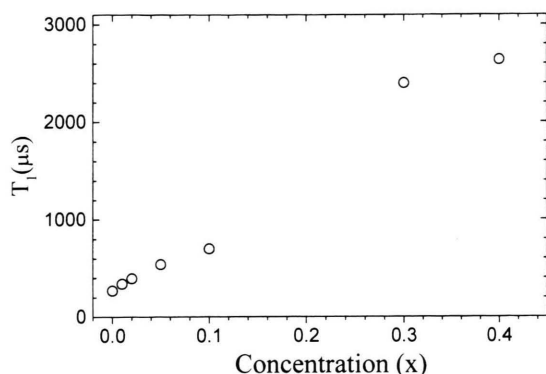


Fig. 6. Spin-lattice relaxation time as a function of impurity concentration  $K_2Sn_{1-x}Re_xCl_6$  at room temperature.

### 2.2. Relaxation Data

At room temperature,  $^{35}Cl$  relaxation is determined in  $K_2SnCl_6$  mainly by the hindered rotation of  $SnCl_6$ -octahedra which is characterized such that the value of  $T_1$  and  $T_2$  have the same order as the characteristic time of reorientational motions in an octahedron. Thus  $T_1$  and  $T_2$  are observed to decrease rapidly above  $T_{cl} = 262$  K with increasing temperature.

On the other hand, in  $K_2ReCl_6$  the on-set temperature of the hindered rotation is higher ( $> 350$  K) than that for  $K_2SnCl_6$ . However, in the paramagnetic phase, the spin-lattice and the spin-spin relaxation times in  $K_2ReCl_6$  are determined mainly by the magnetic transferred hyperfine interaction which is essentially temperature independent and the value of  $T_1$  and  $T_2$  is smaller by an order than those for  $K_2SnCl_6$ .

Figure 6 shows the spin-lattice relaxation time as a function of Re-concentration for the  $K_2SnCl_6$ -structure in  $K_2(Sn-Re)Cl_6$  at room temperature.  $T_1$  increases systematically as the Re-concentration increases. Comparing the fact that  $T_1$  decreases with increasing temperature to the increase in  $T_1$  with Re-concentration points out that the temperature region for the hindered rotation is shifted to higher temperatures by the substitution of the Re-impurities. This result is in agreement with the result obtained from the VCA-model of eq. (1); The transition temperature in  $K_2SnCl_6$ -structure decreases gradually with the increase of the Re-concentration.

### 3. Summary

$K_2Sn-ReCl_6$  exhibits typical features of mixed isomorphous hexahalometallates possesses. They are characterized by the shift of the temperature range of anomalous lattice dynamics. The shift of the transition temperature can be described by an empirical formula based on the VCA-model. The impurity effects in the isomorphous system are caused by the static distribution of the guest ions at the corresponding counterpart lattice sites.

Compared to the impurity effects in the  $K_2SnCl_6$ -structure, the effects in the  $K_2ReCl_6$ -structure is masked by the fast electronic fluctuation caused by the transferred hyperfine interaction leading to the absence of the satellite lines. Such a shielding effect of the exchange interaction affects also the NQR relaxation such that the rate of relaxation is slowed down with increasing Re-content.

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