Successive Phase Transitions in Potassium Hexachloroselenate(IV) Revealed by ^{35}Cl NQR*

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K_2SeCl_6 undergoes structural phase transitions of first order at 35 K, 65 K, and 79 K. The temperature dependence of the ^{35}Cl NQR spin-lattice relaxation time suggests that the phase transitions at 65 K and 79 K are displacive ones associated with a resonant soft mode. The presence of a precursor cluster is suggested by the temperature dependence of the signal intensity above 79 K.

Key words: Phase transition, Soft mode, NQR, Spin-lattice relaxation.

1. Introduction

Cubic antifluorite crystals R_2MX_6 undergo two types of phase transitions [1, 2]. K_2OsCl_6 and K_2ReCl_6 belong to type I, in which the temperature dependence of the halogen NQR frequencies is nearly continuous through the transition temperature and the center of mass of the NQR frequencies is not conserved; that is, the weighted average of the NQR frequencies in the low-temperature phase does not coincide with the frequency extrapolated from the high-temperature phase. On the other hand $(NH_4)_2PtBr_6$ and Rb_2PtI_6 belong to type II, in which the phase transition is discontinuous and the center of mass of the NQR frequencies is conserved. In type I the soft mode is a rotary lattice vibrational mode of the complex anion with T_{1g} symmetry, while in type II the symmetry of the soft mode is E_g and the low-temperature structure is associated with no static rotation of the complex anion. In the present study it is shown that K_2SeCl_6 exhibits successive phase transitions very similar to those of K_2ReCl_6, which undergoes a ferro-rotative transition at 111 K, a further antiferro-rotative transition at 103 K, and another structural transition at 76 K [3]. Although phase transitions of K_2ReCl_6 have been extensively studied by crystallographic and spectroscopic experiments [3], spin-lattice relaxation time measurements of NQR have provided no information concerning the dynamics of structural phase transitions because K_2ReCl_6 is paramagnetic. In the following, the dynamics of transitions in K_2SeCl_6 is discussed by use of the results of ^{35}Cl NQR spin-lattice relaxation time measurements.

2. Experimental

Yellow crystals of K_2SeCl_6 were prepared by passing HCl gas through a 12 N hydrochloric acid solution containing H_2SeO_3 and KCl with molar ratio 1 : 2 [4, 5]. The crystals were dried in a dry HCl gas stream and sealed into a glass tube with He gas for heat exchange. A pulsed spectrometer [6] based on the Matec gated amplifier 515A was used. Fourier transformed (FT) power spectra were obtained by use of an Iwatsu SM-2100C FFT signal analyzer. The ^{35}Cl NQR frequency was determined by recording the FT spectra and/or by plotting the echo amplitude as a function of the carrier frequency. The spin-lattice relaxation time T_{1Q} was determined employing the $\pi - \tau - \pi/2 - \tau_e - \pi$ pulse sequence, where the spacing time τ was varied while τ_e was set constant (ca. 150 μs). The error of

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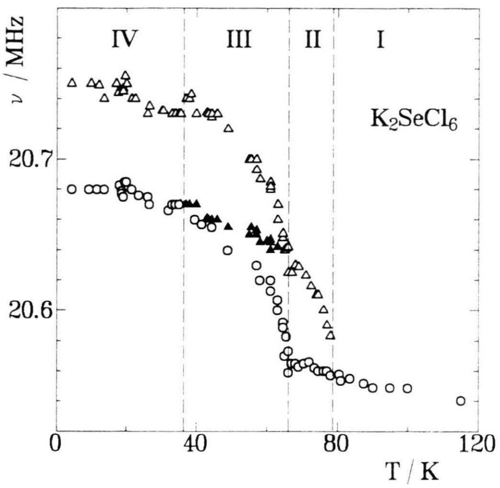

Fig. 1. Temperature dependence of the ^{35}Cl NQR frequencies of K_2SeCl_6.

Table 1. ^{35}Cl NQR frequencies ν of K_2SeCl_6 at several temperatures.

T / K	ν / MHz		
4.2	20.7510±0.0005	20.68 ±0.005	
63	20.672 ±0.001	20.645 ±0.001	20.600±0.001
77.3	20.5899±0.0005	20.5598±0.0005	
291.5	20.4340±0.0005		

the T_{1Q} measurements is estimated to be ca. ± 10 %. The sample temperature was controlled using an electronic controller (Ohkura EC-61A and Oxford DTC 2 for above and below 77 K, respectively) or a mechanical manostat (pumping liquid N_2) and measured with an accuracy of ± 0.5 K by copper-constantan and gold + 0.07% iron-chromel thermocouples above and below 77 K, respectively. The precision of temperature control (temperature inhomogeneity accross the sample) was estimated to be within ± 0.3 (0.6) K, ± 0.2 (0.4) K, and ± 0.05 (0.05) K at around 35 K, 65 K, and 79 K, respectively.

3. Results

Figure 1 shows the temperature dependence of ^{35}Cl NQR frequencies of K_2SeCl_6. There appear successively four crystal phases I, II, III, and IV with decreasing temperature. In 1963, by use of a superregenerative spectrometer, D. Nakamura et al. [4] reported for K_2SeCl_6 a single ^{35}Cl NQR line at liquid N_2 temperature. However in the present investigation it was found that this NQR signal consists of two closely separated lines.

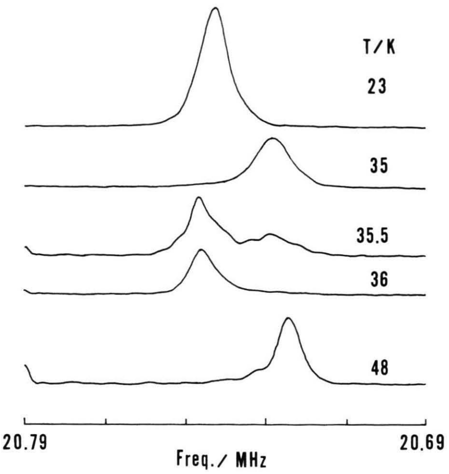

Fig. 2. Temperature dependence of FT power spectra of the high-frequency lines through the phases IV-III.

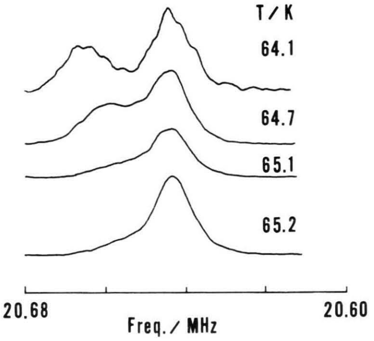

Fig. 3. Temperature dependence of FT power spectra of the high-frequency lines through the phases III-II.

The resonance frequencies at several temperatures are listed in Table 1. The FT power spectra measured in the vicinity of each phase transition point are shown in Figures 2 - 5. The resonance frequencies determined by the FT spectra are in Figs. 6-9 as functions of temperature. The low-frequency line in phase IV tended to be saturated rather easily, so that it was difficult to determine the frequency precisely by use of the FT spectra. The temperature dependence of the ^{35}Cl NQR spin-lattice relaxation time T_{1Q} is depicted in Figure 10.

4. Discussion

As shown in Figs. 2 and 6, a new resonance component appears abruptly at ca. 20 kHz to the high-

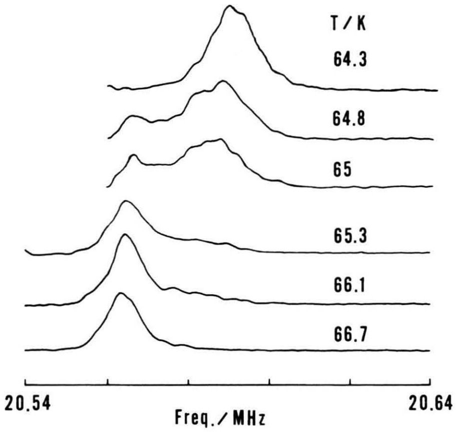

Fig. 4. Temperature dependence of FT power spectra of the low-frequency lines through the phases III-II.

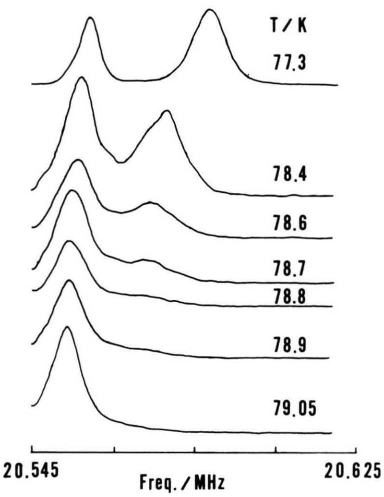

Fig. 5. Temperature dependence of FT power spectra of the ^{35}Cl NQR lines through the phases II-I.

frequency side when the temperature is increased beyond 35 K, indicating that the IV-III phase transition is of first order. The discontinuities observed in the temperature dependence of the resonance frequencies shown in Figs. 7-9 indicate that the III-II and II-I phase transitions are also first order ones in the strict sense. The IV-III, III-II, and II-I phase transition temperatures were determined as 35 K, 65 K, and 79 K, respectively. In phase II, the high-frequency line is twice as intense as the low-frequency one. The temperature dependence of the FT spectra at the II-I phase transition can be interpreted by assuming that the signal of phase I grows with increasing

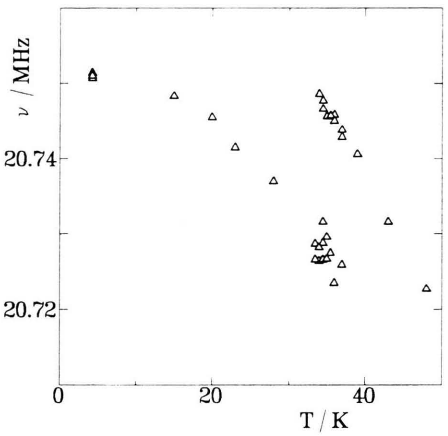

Fig. 6. Temperature dependence of the ^{35}Cl NQR frequencies (high-frequency lines) through the phases IV-III.

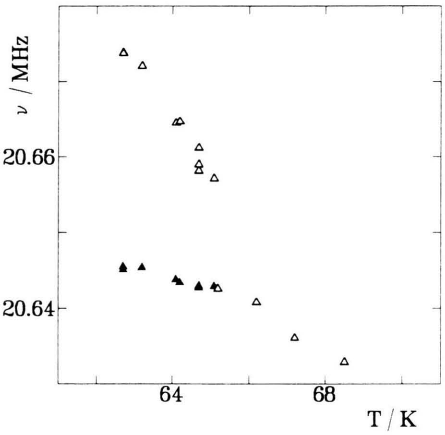

Fig. 7. Temperature dependence of the ^{35}Cl NQR frequencies (high-frequency lines) through the phases III-II.

temperature, while that of phase II disappears (see Figure 5). The signals of both phases coexist over a temperature range of ca. 0.5 K, which is much wider than the temperature inhomogeneity accross the sample (ca. 0.05 K). The temperature dependence of the resonance frequencies observed in K_2SeCl_6 is very similar to that in K_2ReCl_6 [3], in which a ferrorotative and an antiferro-rotative transition associated with static rotation of complex anions, and another structural transition occur successively. Defining the axis of the static rotation as z and the plane perpendicular to z as xy plane, the high- (twice intense) and low-frequency lines observed in phase II can be assigned to chlorines on the xy plane and the z axis, respectively.

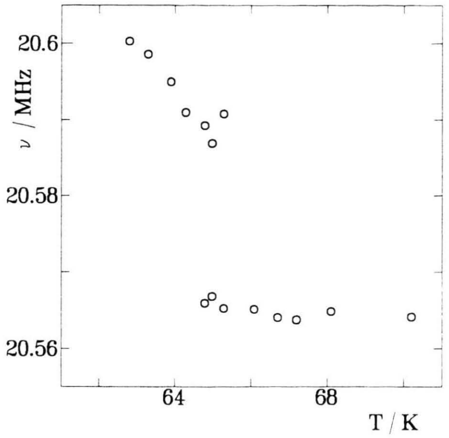

Fig. 8. Temperature dependence of the ^{35}Cl NQR frequencies (low-frequency lines) through the phases III-II.

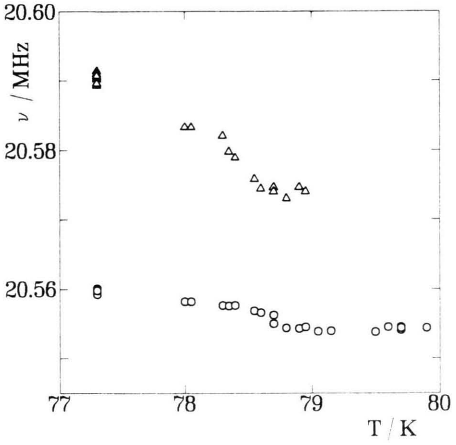

Fig. 9. Temperature dependence of the ^{35}Cl NQR frequencies through the phases II-I.

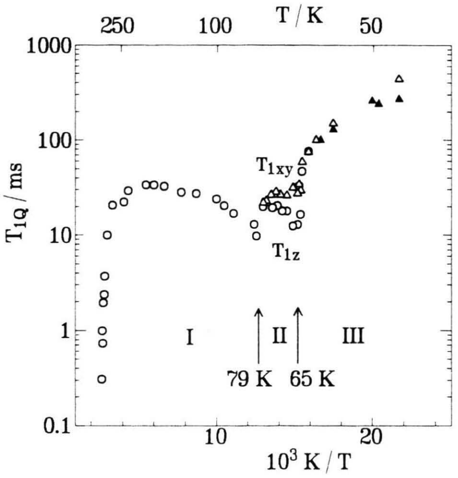

Fig. 10. Temperature dependence of the ^{35}Cl NQR spin-lattice relaxation times T_{1Q} of K_2SeCl_6.

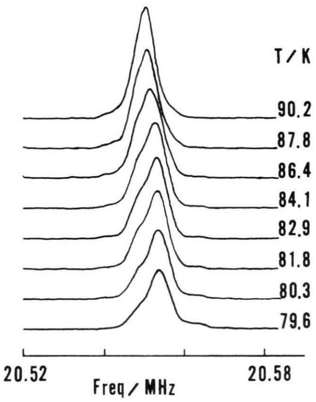

Fig. 11. Temperature dependence of FT power spectra of the ^{35}Cl NQR lines above the II-I phase transition point.

Beside the temperature dependence of ^{35}Cl T_{1Q} shown in Fig. 10, ^{37}Cl T_{1Q} was also measured in the temperature range above 80 K. The ratio of $T_{1Q}(^{37}Cl)/T_{1Q}(^{35}Cl)$ was found to be 1.0 ± 0.2 and 1.6 ± 0.2 above and below ca. 300 K, respectively. The latter value agrees well with the square of the ratio of the quadrupole moments, $[Q(^{35}Cl)/Q(^{37}Cl)]^2 = 1.61$, which means that the nuclear relaxation is governed by quadrupolar relaxation due to lattice vibrations. The rapid decrease of T_{1Q} observed above ca. 300 K is explained by the onset of a reorientational motion of the complex anion. From the slope of the log T_{1Q} vs. T^{-1} curve, the activation energy of 72 kJ mol^{-1} was obtained. T_{1Q} shows minima at 65 K and 79 K as shown in Fig. 10, indicating softening of lattice vibrations. The phase transitions at 65 K and 79 K are expected to be displacive ones associated with static rotation of complex anions. T_{1Q} of chlorines on the *xy* plane, T_{1xy}, is longer than T_{1Q} of chlorines on the *z* axis, T_{1z}, in phase II. This suggests that the librational fluctuations are nearly isotropic in the present complex, since theoretically $T_{1xy} = 2T_{1z}$ is expected by assuming isotropic librations [7,8]. As the temperature approaches the II-I transition point, T_{1xy} becomes closer to T_{1z}, which suggests that the librational fluctuation about the *z* axis is appreciably enhanced at the transition.

The presence of a precursor cluster, as claimed in K_2OsCl_6 [9], was suggested from the temperature

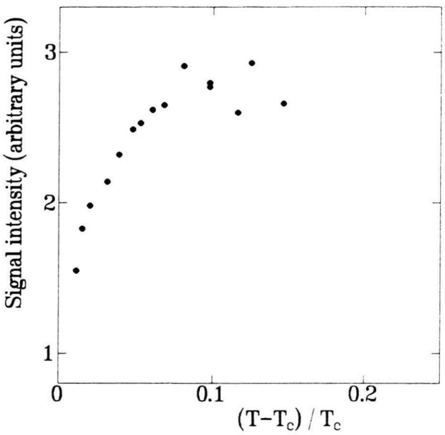

Fig. 12. Signal intensity, (linewidth) × (spectral height), as a function of the reduced temperature above the II-I phase transition point T_c.

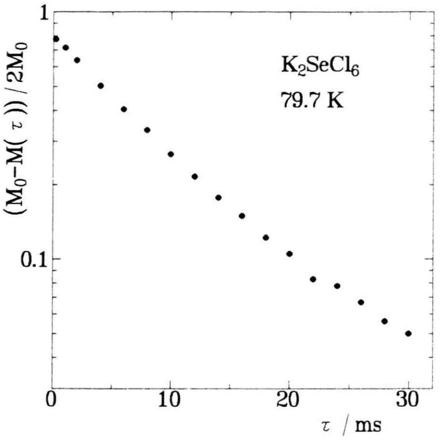

Fig. 13. Recovery curve of the ^{35}Cl magnetization $M(\tau)$ of K_2SeCl_6 at 79.7 K. M_0 denotes the equilibrium magnetization.

dependence of the signal intensity above 79 K. As shown in Fig. 11, the linewidth of the FT spectra is almost independent of temperature while the spectral height decreases appreciably. In Fig. 12, the signal intensity, (linewidth) × (spectral height), is plotted as a function of the reduced temperature. The signal intensity of the high-temperature phase I shows an appreciable decrease when the temperature is lowered toward the II-I phase transition point. This result seems to be consistent with the picture that precursor clusters of the low-temperature phase grow in the high-temperature phase with decreasing temperature to the phase transition point. As for the precursor effect, it has been reported for K_2OsCl_6 that two relaxation components must be introduced for the ^{35}Cl magnetization recovery just above the tetragonal-cubic transition temperature [10]. However, the recovery curve of the ^{35}Cl magnetization in K_2SeCl_6 at 79.7 K could be explained by a single exponential function as shown in Figure 13. This difference may be associated with the difference of the dynamic nature of the tetragonal precursor in the cubic phase.

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