

NQR Pressure Studies of Molecular Dynamics and Phase Transitions.

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Abstract.

High pressure technique applied in studies of NQR frequency and quadrupole relaxation has been used for deriving information on the dynamical properties of crystals and the nature of their phase transitions. The ^{35}Cl NQR pressure studies have been carried out and a detailed analysis is given for the following topics: 1) Symmetric and asymmetric hydrogen bonded systems under high pressure. 2) NQR pressure studies of the system with soft zone-center optic phonons.

I. Introduction.

The radiospectroscopy of magnetic resonances for samples exposed to a high hydrostatic pressure plays a particular role in studies of electronic structure of molecules, molecular dynamics and phase transition phenomena in solids. Pressure, used as a second thermodynamic variable (besides temperature), allows one to achieve a more complete description of molecular motion and phase transitions. The util-

ity and significance of the high pressure NQR are demonstrated on the basis of some selected results recently obtained in our laboratory.

II. Symmetric and asymmetric hydrogen-bonded systems under high pressure.

Many crystalline materials contain pairs of oxygen atoms connected by hydrogen bonds. By lowering the temperature some of these substances undergo order-disorder phase transformations to states of spontaneously broken symmetry characterized by long-range proton order. An interesting structural correlation has been known for many years concerning hydrogen bonds connecting oxygen atoms in crystals at ordinary pressures. Specifically this correlation shows that covalent O-H bond lengths stretch as $R_{\text{O}\dots\text{O}}$, the distance between hydrogen-bonded oxygens, decreases (Fig. 1). The relation between the distance of the electronegative atoms $R_{\text{O}\dots\text{O}}$ and the oxygen-proton distance $R_{\text{O}-\text{H}}$ as well

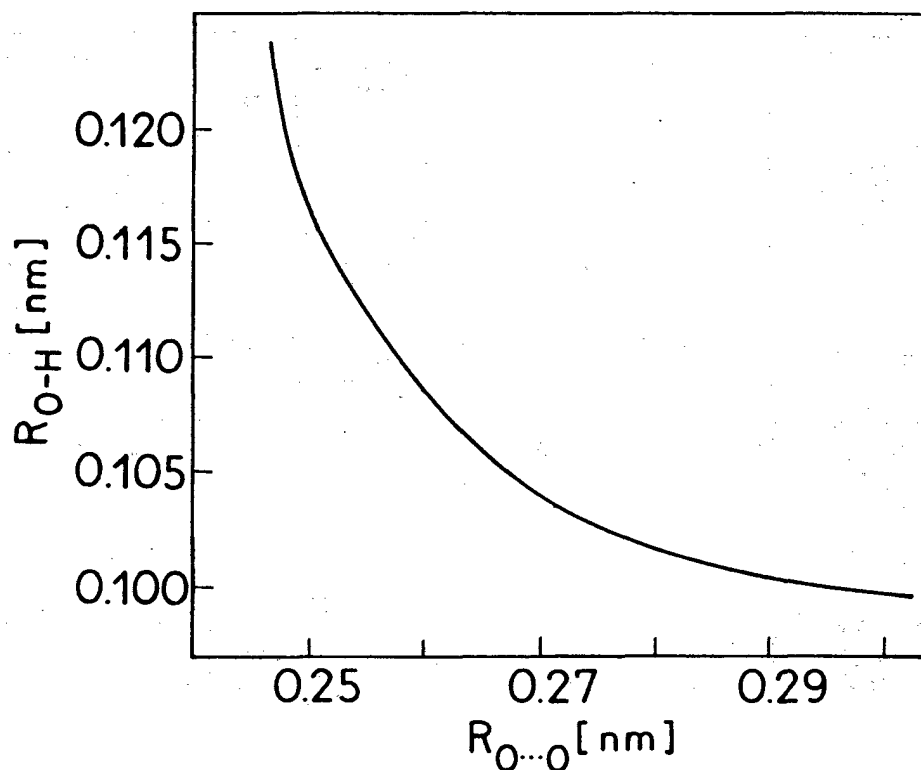


Figure 1: Theoretical dependence of the proton-oxygen distance R_{O-H} on the hydrogen bond length $R_{O...O}$ as calculated from the Matsushita and Matsubara model. Tunnelling process has been taken into account.

as the proton tunnelling effect have been explained by Matsushita and Matsubara (1). In particular the data indicate that when the participating oxygens are as close, or closer than about 0.24 nm the hydrogen should be found at the midpoint position. These observations suggest that if pressure were applied to substances containing hydrogen-bonded oxygens so as to vary the relevant oxygen separation, the same correlation should obtain. This pressure behaviour leads to a significant reduction of the potential barrier separating the two equivalent minima and hence to an increase of quantum fluctuations via tunnelling.

Variations of the proton localisation in the hydrogen bond are reflected by changes of the electric field gradient EFG and therefore by changes of the NQR frequency. The NQR spectroscopy as being particularly sensitive to subtle changes in electron density, is a valuable tool in studies of hydrogen bonds in the solids. Application of a relatively small hydrostatic pressure of order of several hundred MPa causes considerable changes in the NQR frequency observed also for nuclei located outside the hydrogen bond. Our recent NQR pressure stud-

ies of hydrogen bonded complexes have shown that the sign and magnitude of the pressure coefficient of the NQR frequency is related to the degree of proton transfer in the hydrogen bond (2).

The pressure induced variations of the electronic structure of the hydrogen bonded systems were monitored at the opposite ends of the hydrogen bond in the following systems: a) pentachlorophenol-2-chlor-pyridine complex, b) ferroelectric phase of ammonium hydrogen bis chloracetate $NH_4H(ClCH_2COO)_2$, c) ferroelectric phase of tetramethylammonium hydrogen di-trichloroacetate $N(CH_3)_4H(CCl_3COO)_2$. The obtained results are shown in Fig. 2. With increasing pressure the distance between hydrogen bonded oxygens decreases. The proton moves towards the center of the bond. Therefore, the pressure coefficient of the NQR frequency is negative for the monitoring chlorine nucleus at the one side of the hydrogen bond (R_{O-H} increases) and positive for the chlorine at the opposite side ($R_{H...O}$ decreases). The observed pressure dependences of the NQR frequency reflect the pressure induced proton motion in the hydrogen bond and may be explained by the theory of Matsushita

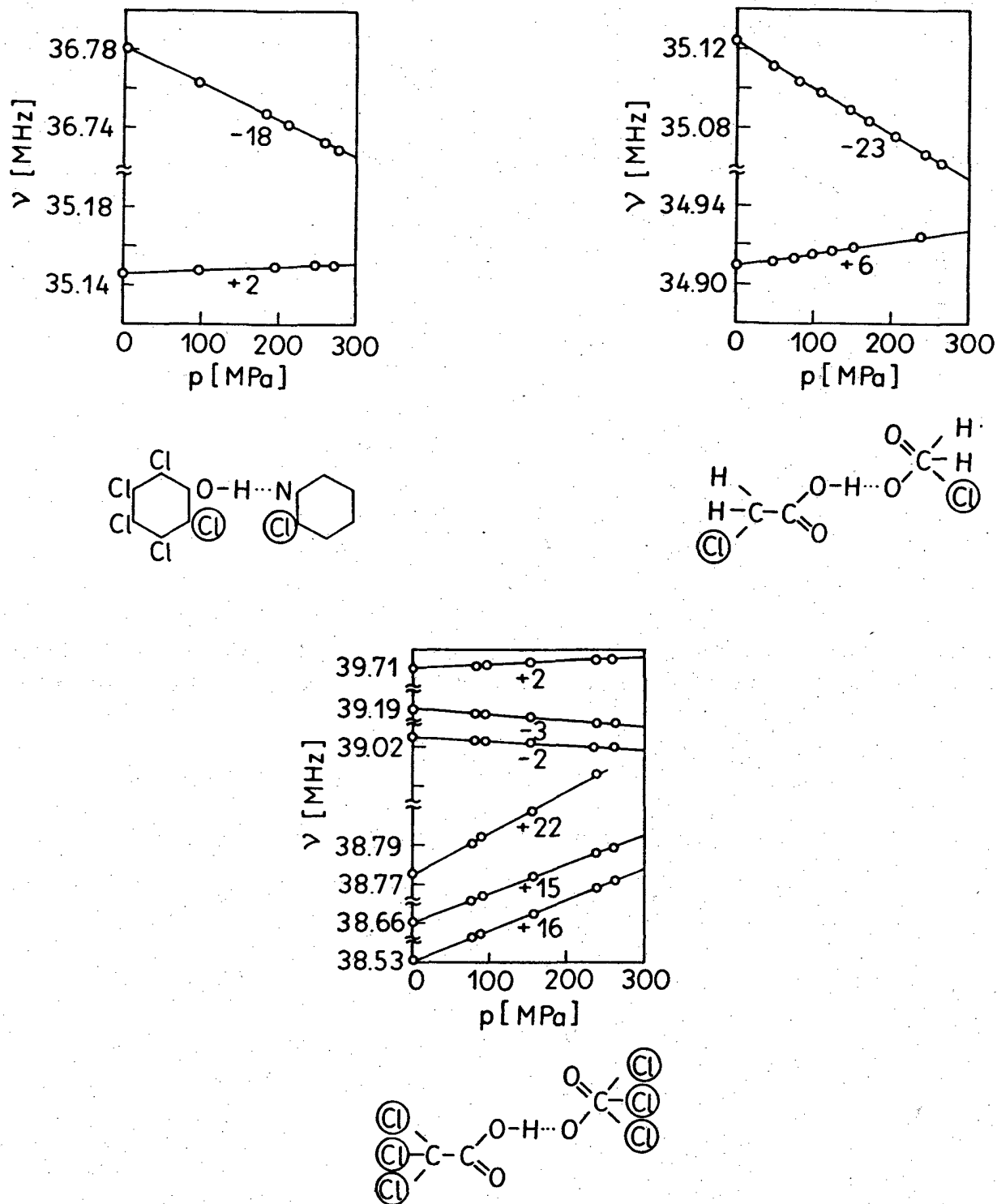


Figure 2: Pressure dependences of the ^{35}Cl NQR frequency in molecular systems with asymmetric hydrogen bonds monitored on both sides of the bond. a) complex of pentachlorophenol-2-chlor-pyridine, b) ferroelectric phase of ammonium hydrogen bischloracetate $\text{NH}_4\text{H}(\text{ClCH}_2\text{COO})_2$, c) ferroelectric phase of tetramethylammonium hydrogen di-trichloro-acetate $\text{N}(\text{CH}_3)_4\text{H}(\text{CCl}_3\text{COO})_2$. The values of pressure coefficients of the NQR frequency $\partial\nu/\partial p$ are expressed in kHz/100 MPa. All measurements were carried out at 77 K.

and Matsubara (1).

The pressure behaviour of the hydrogen bonded molecular systems with the monitoring chlorine nuclei on both sides of hydrogen bonds are different for asymmetric and short symmetric bonds. $(\text{CCl}_3\text{COO})_2$ HK belongs to a group of hydrogen bonded molecular systems with short symmetric hydrogen bond. The crystal is composed of K^+ ions and two trichloroacetate radicals kept together by a short symmetric hydrogen bond $(\text{Cl}_3\text{CCOO} \dots \text{H} \dots \text{OCCCl}_3)^-$. The substitution of the bonding proton in dimer ion for deuterium gives no changes in the NQR frequency. It proves the symmetry of hydrogen bond as well as equivalency of the all CCl_3 groups in the crystal lattice. Temperature dependences of the ^{35}Cl NQR frequency and quadrupolar spin-lattice relaxation time T_1 of ^{35}Cl nuclei at atmospheric pressure are shown in Fig. 3. There are two additive mechanisms of the quadrupolar spin-lattice relaxation:

$$\frac{1}{T_1} = a T^n + b \exp(-E_a/RT) \quad (1)$$

where R - gas constant, $E_a = 34.4 \text{ kJ mol}^{-1}$ - activation energy, a , b , n - constant values $a = 6.6 \cdot 10^{-3} \text{ s}^{-1}\text{K}^{-2}$, $b = 3.7 \cdot 10^{12} \text{ s}^{-1}$, $n = 1.89$. At low temperature the relaxation process is characterized by the first part of equation 1 which describes the influence of torsional vibrations with small amplitudes on the relaxation time. At higher temperatures from about 170 K the hindered rotation of the CCl_3 -groups starts to dominate. The $T_1(T)$ dependence is then described by the exponential part of equation 1.

Our pressure studies have shown that the average pressure coefficient of the NQR frequency is equal to zero for such a symmetric system. The crystal is not stable and some polymorphic transitions were induced by high pressure. By applying initial pressure higher than 80 MPa at 77 K the NQR spectrum changes completely, as shown in Fig. 4. When the pressure is higher than 240 MPa three new NQR lines appear in the spectrum in addition to three existing already. The process is reversible and after several hours at normal pressure the NQR spectrum looks like before applying pressure.

III. NQR pressure studies of the system with soft zone-center optic phonons.

Pressure is one of the best, and often the only, variable which can significantly alter crystal potentials and thereby a delicate balance between competing lattice interactions. The decrease of phase transition temperature T_c with increasing pressure can be formally described by the soft-mode theory. In this case the vanishing of the soft-mode frequency ω_S at T_c results from the cancellation of the short-range forces by the Coulomb forces. Formally ω_S is given in the harmonic approximation by the difference between short-range (SR) and long-range (LR) interaction, i.e.,

$$\omega_S^2 \sim [SR_{\text{interact.}} - LR_{\text{interact.}}] \quad (2)$$

In the present work we have studied the influence of hydrostatic pressure on the ^{35}Cl NQR frequency in the vicinity of phase transition in K_2OsCl_6 . The negative pressure coefficient for the transition driven by the softening of the zone centre rotary mode was observed (Fig. 5). The pressure coefficient of the phase transition temperature T_c amounts to $dT_c/dp = -2.2 \cdot 10^{-2} \text{ K MPa}^{-1}$ (3).

High pressure strongly affects the balance between competing forces responsible for soft-mode behaviour in crystals exhibiting displacive structural phase transitions by simply reducing the interionic separations. One can notice that decreasing the interionic distance r by pressure increases the SR interactions ($\sim r^{-n}$, especially when n is large ≈ 10) much more rapidly than the LR interactions ($\sim r^{-3}$) leading to an increase in ω_S and thereby a decrease in T_c . This can be clearly seen on a typical temperature dependence of ω_S ,

$$\omega_S^2 = K(T - T_c) \quad (3)$$

where K is a positive constant. A large value of ω_S at constant T necessitates a lower value of T_c . The experimental pressure dependence of T_c may be used to evaluate the contribution of various electrostatic forces considered in the lattice potential calculations. The halogen-cation overlap repulsion stabilizes the cubic phase, whereas the anion-cation Coulomb forces and the Cl-Cl^- overlap repulsion between halogens of neighbouring OsCl_6^{2-} ions favours

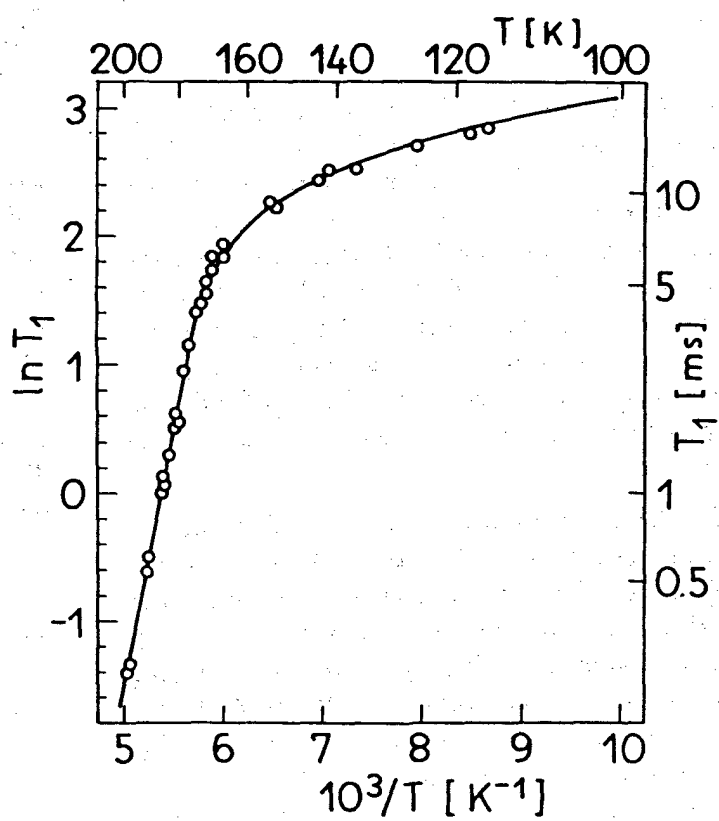
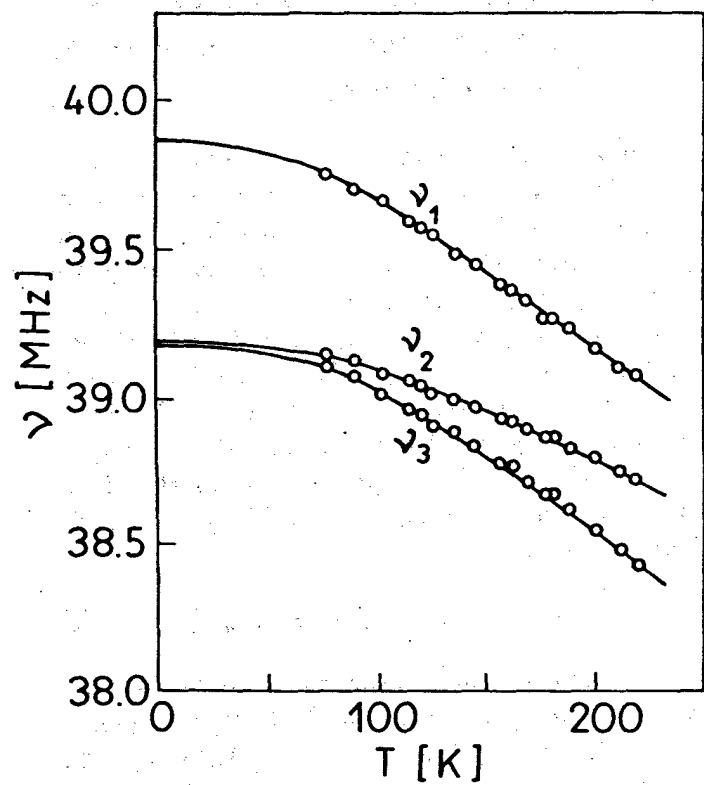


Figure 3: a) Temperature dependence of the ^{35}Cl NQR frequency in $(\text{CCl}_3\text{COO})_2\text{HK}$. b) Temperature dependence of the quadrupolar spin-lattice relaxation time T_1 of ^{35}Cl nuclei in $(\text{CCl}_3\text{COO})_2\text{HK}$.

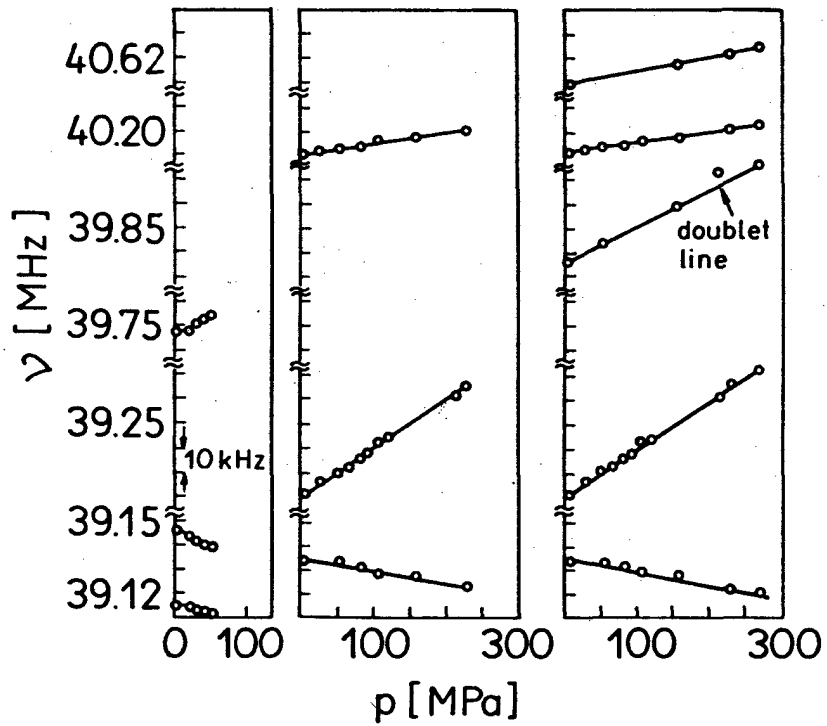


Figure 4: Pressure dependence of ^{35}Cl NQR frequency in $(\text{CCl}_3\text{COO})_2\text{HK}$ while initial pressure is: a) lower than 70 MPa b) between 80 MPa and 240 MPa c) higher than 240 MPa

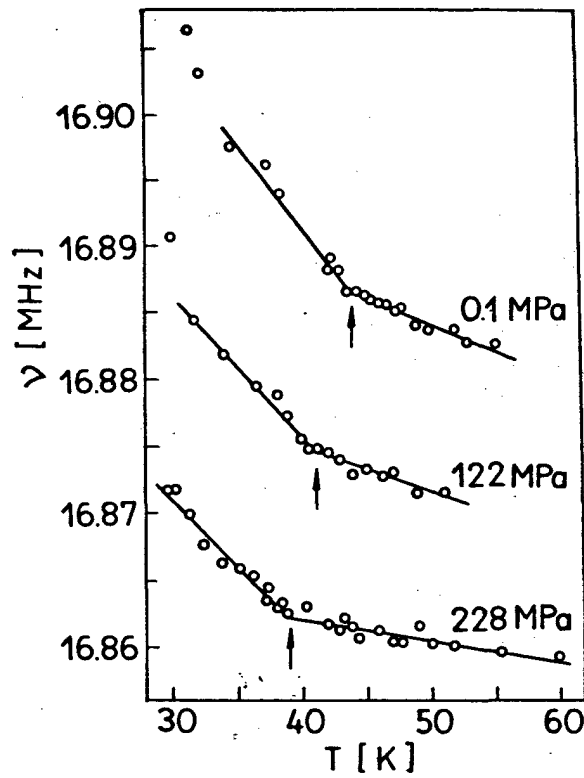


Figure 5: Temperature dependence of the ^{35}Cl NQR frequency in the vicinity of the phase transition in K_2OsCl_6 at some selected pressures.

the rotation of the octahedra. The transition to a tetragonal structure in K_2OsCl_6 is governed by short-range forces. Within the frame of this model the negative pressure shift of T_c may be understood if the Cl-Cl⁻ overlap repulsion increases more rapidly with pressure than the other interactions.

The above results confirm the validity of the Samara rule (4) for the zone centre transitions, in which the negative pressure coefficient of the phase transition temperature is observed without exceptions. However, for the zone boundary transitions the sign of a pressure coefficient depends on a detailed lattice dynamics of a particular compound and either positive or negative pressure coefficient can be observed in this case. This difference in behaviour can be tentatively interpreted in terms of a reversal in the roles of the short-range and long-range forces in the lattice dynamics of the two cases.

Purely displacive phase transitions have been observed in several compounds of the perovskite (RMX_3) and antiferite (R_2MX_6) structures. The two crystal structures are similar and in all cases the purely displacive phase transitions can be described in terms of a reorientation of the equilibrium positions of the MX_6 octahedra combined with a distortion of the R-ion cages in which the octahedra reside. The order parameter for the phase transition is the rotation angle of the $OsCl_6^{2-}$ octahedra with respect to the cubic axes of the crystal. The ferrodistortive rotation of the $OsCl_6^{2-}$ octahedra at T_c transforms the structure of the crystal from space group O_h^5 to a tetragonal symmetry described by the C_{4h}^5 space group. Up to now the high pressure studies for antiferites in the vicinity of their phase transitions were carried out only for K_2SnCl_6 (5) and K_2ReCl_6 (6). For K_2SnCl_6 the Samara rule has been confirmed since a condensation at the zone centre or at the zone boundary is related to a negative or positive pressure coefficient, respectively. However, for K_2ReCl_6 the rule has been fulfilled only for the transition driven by the softening of the zone centre rotary mode.

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