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STRUCTURAL PHASE TRANSITIONS IN QUASI-ONE-DIMENSIONAL JAHN-TELLER CRYSTALS

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Experimental approaches to the structural phase transitions in three quasi-one-dimensional Jahn-Teller crystals $CsCuCl_3$, $RbCrCl_3$ and $CsCrCl_3$ are done by the measurements of the optical birefringence, magnetic susceptibility and EPR absorption. Results are discussed in connection with the distortions of $-CuCl_3-$ (or $-CrCl_3-$) chains and their motions.

1. Introduction

Recent rapid progress in the investigations of magnetic phase transitions in magnetically condensed matter are doubtlessly indebted to the discovery of low-dimensional magnetic substances. This is suggestive of the usefulness of "low-dimensional Jahn-Teller crystals" for understanding the cooperative Jahn-Teller effect. The one-dimensional Jahn-Teller systems are substances which contain Jahn-Teller active ions in structure permitting dominant ion-ion interactions to occur in one direction. The interest in studying the cooperative Jahn-Teller effect in these substances is in the fact that theoretically tractable models can exist with which to compare the observations.

The present work is concerned with three compounds $CsCuCl_3$, $RbCrCl_3$ and $CrCrCl_3$, which belong to a family of crystals described approximately as one-dimensional Jahn-Teller systems and exhibit structural phase transitions caused by the Jahn-Teller effect. In these substances, Cu^{2+} or Cr^{2+} ion is surrounded octahedrally by six Cl^- ions and the $CuCl_6$ (or $CrCl_6$) octahedra form infinite $-CuCl_3-$ (or $-CrCl_3-$) chains along the c-axis of the crystals by sharing faces.

In the present investigation we report the results of measurements of EPR spectra, magnetic susceptibilities and birefringences performed on single crystals of these three compounds, and discuss them in connection with the distortions of $-CuCl_3-$ (or $-CrCl_3-$) chains and their motions.

2. Summary of the Crystal Structures and the Structural Phase Transitions

The crystal structures of the present three compounds are identical to that of $CsNiCl_3$ at high temperatures[1],[2]. $CsCuCl_3$ transforms at about 420 K from the highly symmetric structure to a more complex one which consists of hellically distorted chains of face sharing elongated $CuCl_6$ octahedra separated by Cs^+ ions (see Fig. 1(a))[1],[4]. $RbCrCl_3$ also transforms at 470 K from the $CsNiCl_3$ structure (α-phase) to a monoclinic structure (β-phase: see Fig. 1(b)) and again at about 200 K to a new monoclinic one (γ-phase: see Fig. 1(c))[2],[3]. $CsCrCl_3$ transforms only once at about 170 K to a monoclinic (γ-phase) which is identical to γ-structure in $RbCrCl_3$[3],[5]. The experimental studies on the transition at 420 K in $CsCuCl_3$ have been thoroughly done using a variety of techniques[6],[7], but very few studies have been reported on $RbCrCl_3$ and $CsCrCl_3$[5].

3. Experiments and Results

The optical birefringences Δn for $CsCuCl_3$, $RbCrCl_3$ and $CsCrCl_3$ were measured by the Sénarmont method using the light beam of a He-Ne laser at 0.6328μm. The result for $CsCuCl_3$ has been reported in reference [8] and the results for $RbCrCl_3$

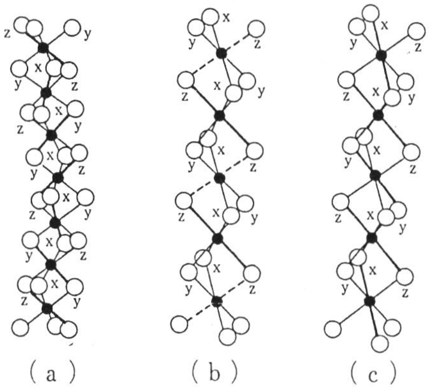

Fig. 1 Perspective views of the distorted linear chains of face-sharing octahedra in, (a) the low-temperature phase of $CsCuCl_3$, (b) the β-phase of $RbCrCl_3$ and (c) the γ-phase of $RbCrCl_3$ and $CsCrCl_3$. The thick and dotted lines represent elongated and compressed axes of octahedra, respectively. The coordinates x, y, z denote the three principal axes of an octahedron.

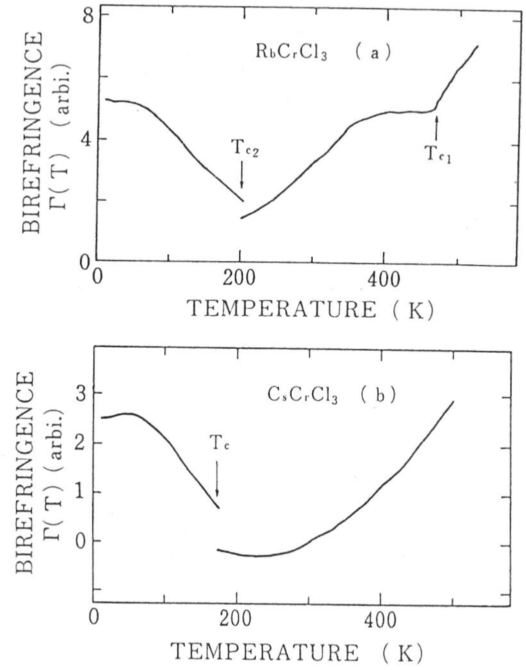

Fig. 2 The temperature dependences of the optical birefringences in (a) $RbCrCl_3$ and (b) $CsCrCl_3$ where Γ(T) means the retardation proportional to the optical birefringence Δn.

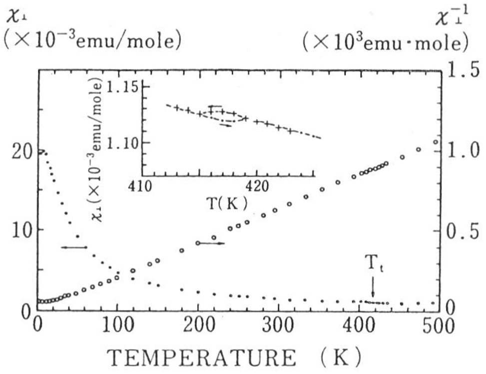

Fig. 3 Susceptibility $\chi_\perp$ and inverse susceptibility $\chi_\perp^{-1}$ measured perpendicular to the c-axis. Insert shows precise behaviour of $\chi_\perp$ around T_t.

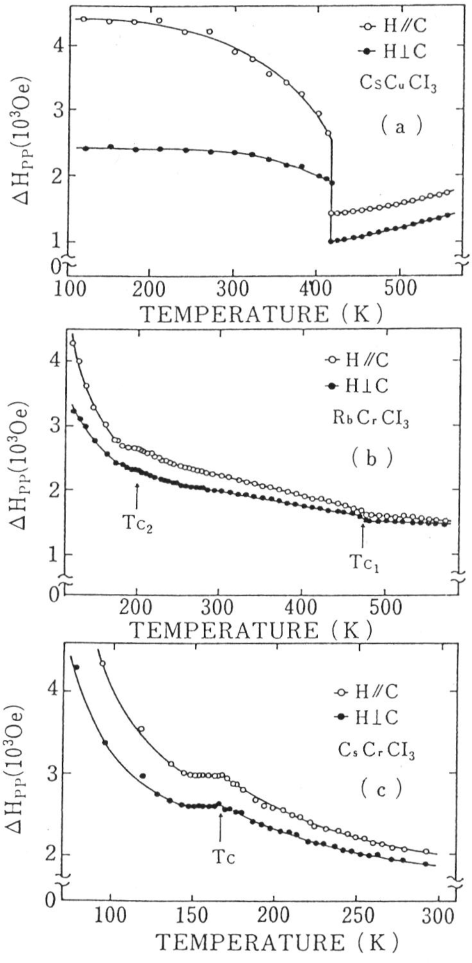

Fig. 4 Temperature dependences of the peak-to-peak derivative linewidths ΔH_{pp} in (a) $CsCuCl_3$, (b) $RbCrCl_3$ and (c) $CsCrCl_3$ in X-band.

and $CsCrCl_3$ are shown in Fig. 2. A sudden change of Δn of $CsCrCl_3$ caused by the structural phase transition was found at 420.0 K ($=T_t$) in a heating run. The thermal hysteresis was recognized to be about 5 K[8]. In the case of $RbCrCl_3$ anomalies in Δn were observed at 469.1 K ($=T_{c1}$) and 197.0 K ($=T_{c2}$). Since the change in Δn at T_{c1} is continuous, the transition at T_{c1} seems to be of a second order. As for $CsCrCl_3$ a discontinuous change in Δn found at 171.6 K in a heating run. The increases of Δn in $RbCrCl_3$ and $CsCrCl_3$ with decreasing temperature are due to the contributions of the antiferromagnetic short-range orders.

Magnetic susceptibilities of $CsCuCl_3$ were measured by the Faraday method at 10 KOe. Figure 3 shows the magnetic susceptibility $\chi_\perp$ perpendicular to the c-axis after the correction of the diamagnetism due to core electrons. From these experimental data we can estimate the exchange interaction J between Cu^{2+} ions neighboring in a chain to be $J/k=24$ K[9] below T_t. When the temperature was risen from room temperature, abrupt increase in $\chi_\perp$ was observed as seen in insert. These facts indicate that the magnitude of the ferromagnetic exchange interaction J above T_t is larger than that below T_t.

The EPR spectra for $CsCuCl_3$, $RbCrCl_3$ and $CsCrCl_3$ were measured in X-band (∿9GHz) frequencies. The first derivatives of absorption lines with considerably broad widths of the order of 10^3 Oe were observed in each compound. The temperature dependences of the peak-to-peak derivative widths ΔH_{pp} in these three compounds are shown in Fig. 4 for the orientations $H/\!/C$ and $H\perp C$. The anisotropies of ΔH_{pp} in these three compounds were found to agree with the $(A+B\cos^2\theta)$ dependence in every phase where θ is the angle between H and the c-axis. As shown in Fig. 4(a) the discontinuous changes of ΔH_{pp} in $CsCuCl_3$ due to the structural transformation were found at about 420 K. However the essential difference between EPR spectra below T_t and those above T_t is only in the magnitude of ΔH_{pp}. These facts are true of $RbCrCl_3$ and $CsCrCl_3$. Hence we can conclude that the almost static local distortions of lattice persist in the high-temperature phases of these three compounds, because the magnetic anisotropies such as the Dyaloshinsky-Moriya interaction which is dominant for ΔH_{pp} in $CsCuCl_3$[10] or the single ion anisotropy which is dominant for ΔH_{pp} in $RbCrCl_3$ and $CsCrCl_3$[11] reflect sensitively the local symmetries around magnetic ions.

4. Dynamical Properties of the Linear Chain and Structural Phase Transitions

In this section, we present a simple model of the above mentioned almost static local distortions of lattice and discuss the mechanism leading to the formation of unique structures as shonw in Fig. 1. The potential energy for such single Jahn-Teller complex as $CuCl_6$ or $CrCl_6$ is now wellknown and expressed using the plane polar coordinates as

$$U = \frac{K}{2}\rho^2 - |A|\rho + B\rho^3\cos 3\theta \tag{1}$$

with $Q_2=\rho\sin\theta$, $Q_3=\rho\cos\theta$, where Q_2 and Q_3 are the normal coordinates of E_g mode of the octahedron, K the lattice force constant, A the linear Jahn-Teller coupling coefficient, B the anharmonic lattice force constant[12]. In $CsCuCl_3$, $RbCrCl_3$ and $CsCrCl_3$ B is negative, because the complexes of $CuCl_6$ and $CrCl_6$ are elongated along one of their axes at sufficiently low temperature. Here we assume the strong Jahn-Teller coupling case in which each octahedron constituting linear chain in the present system is on the bottom of the potential U. In this situation the anharmonic term of the potential U whose magnitude is estimated to be several hundred Kelvin[13] plays an important role in a phase transition or lattice dynamics. As seen from the low-temperature structure shown in Fig. 1, the strong interaction between neighboring octahedra restricts the directions of the tetragonal distortion of neighboring octahedra. Then by taking the coordinate system on successive octahedra as shown in Fig. 1, we introduce a harmonic potential $(C/2)\{\theta_j-\theta_{j+1}-(2\pi/3)\sigma_j\}^2$ between j-th and (j+1)-th octahedra, where C is the force constant and σ_j means the pseudo-Ising spin and has the value ±1. Furthermore we consider a potential $-2J_{ij}\sigma_i\sigma_j$ between σ_i and σ_j in a chain, where J_{ij} is the coupling constant. Therefore the total Hamiltonian of the linear chain of octahedra in the present system is expressed adding the kinetic energy as follows:

$$\mathcal{H} = \sum_j [\frac{1}{2}\mu(\dot{\rho}_j^2 + \rho_j^2\dot{\theta}_j^2) + \frac{K}{2}\rho_j^2 - |A|\rho_j + B\rho_j^3\cos 3\theta_j + \frac{C}{2}(\theta_j - \theta_{j+1} - \frac{2}{3}\pi\sigma_j)^2 - \sum_i J_{ij}\sigma_i\sigma_j], \tag{2}$$

where μ is the effective mass of six Cl^- ions. Using this Hamiltonian, the low-temperature structure is classified with the arrangement of pseudo spin σ as shown in table 1.

Table 1.

arrangement of σ	directions of tetragonal distortions of successive octahedra	substance
↑↑↑↑↑↑(ferro)	Z X Y Z X Y Z X Y ···	$CsCuCl_3$
↑↓↑↓↑↓(anti-ferro)	X Y X Y X Y X Y ···	
↑↑↓↓↑↑↓↓	Z X Z Y Z X Z Y ···	$RbCrCl_3$ $CsCrCl_3$

Hence it is considered that the structural phase transitions in the present systems are caused by the long range order of phase θ which is triggered by the ordering of the pseudo-spin σ in consequence of the interchain interaction. Next in order to treat of the propagating motions of deformations of octahedra along the chain in high-temperature phase, we introduce a new parameter ψ_j defined as $\psi_j = \theta_j - \Sigma(2\pi/3)\Sigma\sigma_k$. Furthermore we neglect the small vibration of ρ around the averaged value $\rho_0 = |A|/2\ K$. Then we obtain the classical equation of motion of $-CuCl_3-$(or $-CrCl_3-$) chain as

$$\ddot{\psi}_j - \frac{3B\rho_0}{\mu}\sin 3\psi_j + \frac{C}{\mu\rho_0^2}(2\psi_j - \psi_{j+1} - \psi_{j-1}) = 0. \tag{3}$$

Moreover in continuum approximation this becomes a sine-Gordon equation for the quantity ψ,

$$\frac{\partial^2\psi}{\partial\zeta^2} - \frac{\mu\rho_0^2}{a^2C}\frac{\partial^2\psi}{\partial t^2} = -\frac{3B\rho_0^3}{a^2C}\sin 3\psi, \tag{4}$$

where ζ is the coordinate along the chain and a is the distance between nearest neighboring magnetic ions. The soliton solutions to this sin-Gordon equation are now well known and correspond to travelling domain walls. Therefore we suggest that in the high-temperature phase of the quasi-one-dimensional Jahn-Teller crystals such as $CsCuCl_3$, $RbCrCl_3$ and $CsCrCl_3$, linear chains of distorted octahedra are divided into many domains by travelling domain walls which are connected with the behaviors of ψ and by thermally excited domain walls which are connected with the behavior of the pseudo spin σ. In the case of $CsCuCl_3$, each domain forms a right-handed or a left-handed helix which corresponds to the almost static local distortion of lattice revealed by EPR measurements. This work has been partly supported by a Grant-in Aid for Scientific Research from The ministry of Education, Science and Culture.

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