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Far-infrared Spectra of Low- and High-temperature Phases of $CsCuCl_3$

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Polarized far-infrared reflection spectra of the $CsCuCl_3$ single crystal have been recorded with the electric vector parallel and perpendicular to the c axis at room temperature. Polarized far-infrared transmission spectra have been measured at liquid-nitrogen temperature. The observed spectra have been interpreted using the factor group analysis based on the space group D_6^2. Far-infrared transmission spectra of the powder sample have also been measured over the temperature range from 175 °C to liquid-nitrogen temperature. The spectrum at 175 °C consists of five bands and reveals a typical feature characteristic of the $CsNiCl_3$ structure (D_{6h}^4). The spectral change due to the phase transition has been interpreted based on the structural distortion of the crystal.

A number of double salts of the AMX_3 type, where A and M are univalent and divalent metal ions, respectively, and X is a halogen ion, crystallize in a hexagonal $CsNiCl_3$ structure with the space group D_{6h}^4-($P6_3/mmc$).[1] Almost all of these crystals do not undergo a phase transition down to liquid helium temperature, with the exception of $CsCuCl_3$. $CsCuCl_3$ transforms from the high-temperature $CsNiCl_3$ structure to a more complex one around 423 K[2-4]. According to the crystal structural analysis of the low-temperature phase of $CsCuCl_3$, the displacement of the atoms caused by the phase transition at 423 K can be expressed as the helical distortion around the c axis of the high-temperature structure. In relation to that remarkable structural change of $CsCuCl_3$, the studies on the optical activity, the X-ray and neutron scattering, the dielectric constant and the sound velocity have been made.[5]

From the vibrational spectroscopic point of view, the spectral change at the transition temperature and the relation between the high- and low-temperature spectra are interesting. The infrared spectrum of $CsCuCl_3$ reported so far has been limited to the transmission spectrum of the polycrystalline sample at room temperature by McPherson and Chang.[6] In their study the high-temperature spectrum and the spectral change due to the phase transition have not been remarked. The present paper reports the results of the polarized far-infrared transmission and reflection spectra of a single crystal for the low-temperature phase. The Raman spectrum at low temperature is given as complementary data. The far-infrared transmission spectra of the powder sample have been measured at various temperatures in the range from 175 °C to liquid-nitrogen temperature in order to persue the spectral change due to the structural phase transition.

Crystal Structure and Factor Group Analysis

The structure of the high-temperature phase of $CsCuCl_3$ is the $CsNiCl_3$ type, for which the details of the structure and the factor group analysis are described in our previous paper.[7] The structure of the low temperature phase is a helically distorted structure of the $CsNiCl_3$ structure, with the space group D_6^2 ($P6_122$) or its enantiomorph D_6^3 ($P6_522$), with six formula units in a Bravais primitive cell, as shown in Fig. 1.[8] The factor group for both of the D_6^2 and D_6^3 groups is isomorphous to the point group D_6 and the result of the factor group analysis is summarized in Table 1.

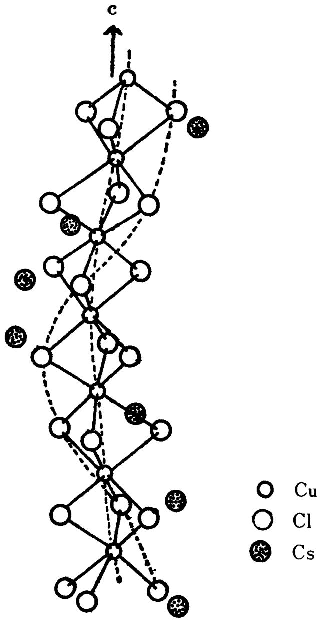

Fig. 1. Crystal structure of the low-temperature phase of $CsCuCl_3$.

Table 1. Factor group analysis for the low-temperature phase of $CsCuCl_3$

D_6	N[a]	T[b]	$N-T$[c]	Activity[d]
A_1	6	0	6	r(XX+YY, ZZ)*
A_2	9	1	8	ir(Z)
B_1	7	0	7	
B_2	8	0	8	
E_1	15	1	14	r(XZ, YZ), ir(X, Y)
E_2	15	0	15	r(XX−YY, XY)

a) Total freedom. b) Acoustic modes. c) Optically active modes. d) r: Raman active modes, ir: infrared active modes.
* X and Y axes are perpendicular, and a Z axis is parallel to the crystallographic c axis, respectively.

Experimental

The powder sample of $CsCuCl_3$ was obtained by evaporation of the hot concentrated aqueous solution of CsCl and

$CuCl_2 \cdot 2H_2O$ in a 1 : 1 mole ratio or in a slight excess of $CuCl_2 \cdot 2H_2O$. The single crystal was grown from a saturated aqueous solution by the temperature difference method. The hexagonal bipyramidal crystal about $7 \times 7 \times 15$ mm^3 in size was obtained after 2 weeks. The plane including the c axis was polished and used for the reflection measurement. The specimen for the transmission measurement is about 0.1 mm thick.

Far-infrared spectra were recorded using a Hitachi 070 far-infrared interferometer equipped with a wire-grid polarizer. For the measurement below 50 cm^{-1}, a high-sensitive liquid-helium cooled germanium bolometer was used as a detector. A Raman spectrum was obtained with a Spex 1401 double monochromator using 647.1 nm excitation from a Kr ion laser.

Results and Discussion

Spectra of the Low-temperature Phase. The polarized far-infrared transmission spectra of a single crystal at liquid-nitrogen temperature are shown in Fig. 2. The polarized far-infrared reflection spectra at room temperature are shown in Fig. 3a. The $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ curves obtained by the Kramers-Kronig analysis are shown in Fig. 3b, where the maxima of $\varepsilon''(\nu)$ give the transverse frequencies. The transmission spectra above 200 cm^{-1} are uninformative, since the absorptions are too strong and saturated. From the maxima of $\varepsilon''(\nu)$ in Fig. 3b, 247 and 279 cm^{-1} are assigned to the A_2 and E_1 modes,

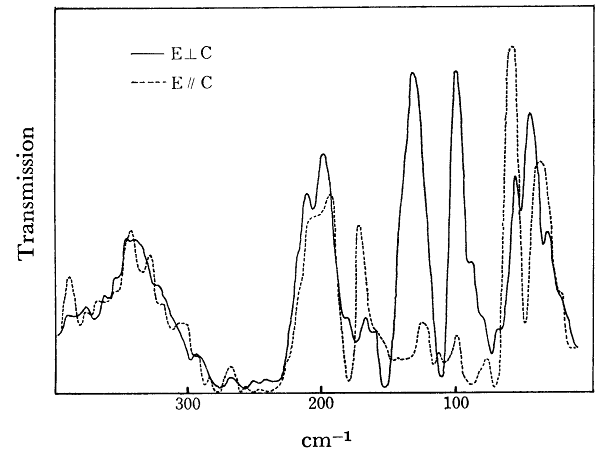

Fig. 2a. Single crystal far-infrared transmission spectra of $CsCuCl_3$ (400—20 cm^{-1}).

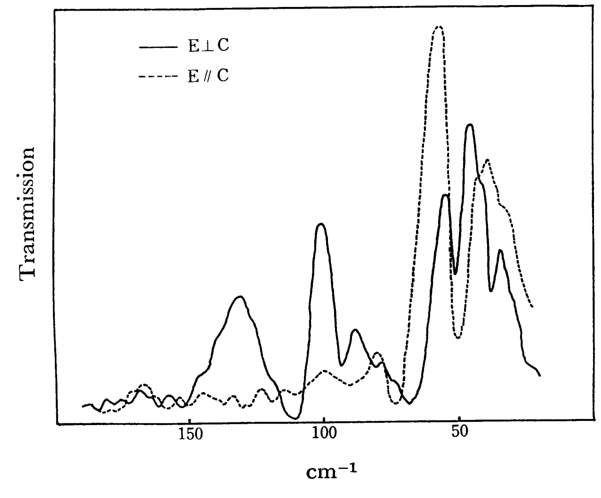

Fig. 2b. Single crystal far-infrared transmission spectra of $CsCuCl_3$ (200—20 cm^{-1}).

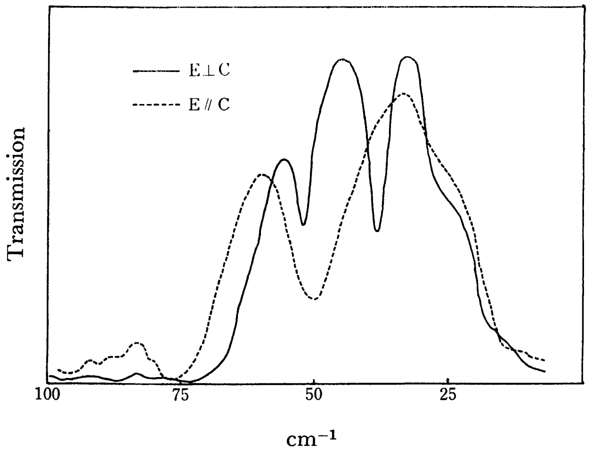

Fig. 2c. Single crystal far-infrared transmission spectra of $CsCuCl_3$ (100—10 cm^{-1}).

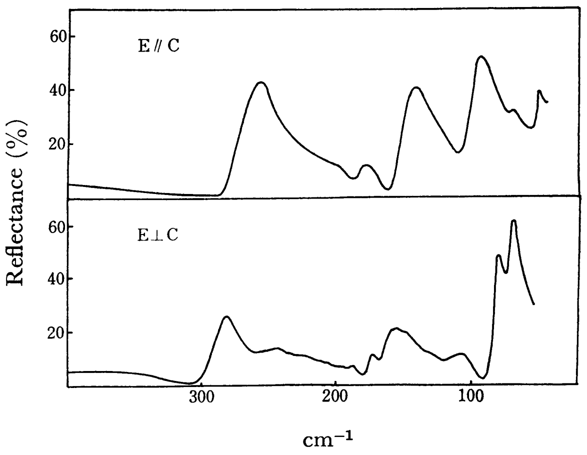

Fig. 3a. Single crystal far-infrared reflection spectra of $CsCuCl_3$.

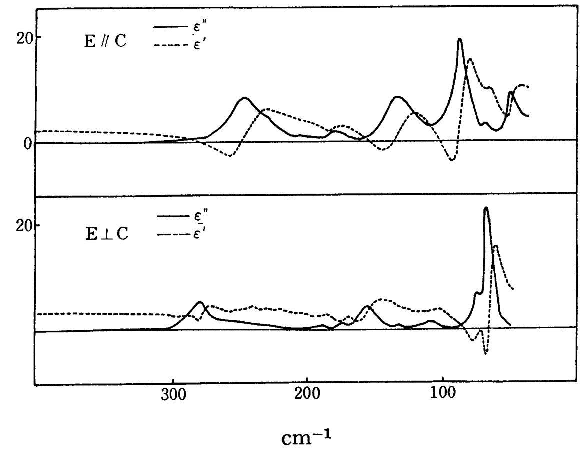

Fig. 3b. $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ obtained from reflection spectra of $CsCuCl_3$.

Table 2. Vibrational frequencies (cm^{-1}) of the low-temperature phase of $CsCuCl_3$

Polarized single crystal spectra				Powder sample spectra Trans.[a]
A_2 species Trans.[a]	(E//C) Ref.[b]	E_1 species Trans.[a]	(E⊥C) Ref.[b]	
*	247	*	279	287
				256
		187	187	188
179	180			180
		174	173	175
		163	157	163
		152		146
140	135			
119				119
		111	111	114
		94		96
90	88			82
		80	76	
72	69			76
		68	68	
		54		52
51	50			
		39		

a) Transmission. b) Reflection.

* Too strong absorption and the frequencies may not be determined.

respectively. In the frequency region below 200 cm^{-1}, the absorption bands at 179, 140, 119, 90, 72, and 51 cm^{-1} are attributed to the A_2 modes, and those at 187, 174, 163, 152, 111, 94, 80, 68, 54, and 39 cm^{-1} to the E_1 modes as shown in Figs. 2a—2c. The $7A_2$ modes and $11E_1$ modes are now determined, while a factor group analysis predicts $8A_2$ and $14E_1$ modes. Table 2 summarizes the observed frequencies obtained from the single crystal transmission and reflection spectra. The frequencies determined by the two different methods agree well, as a whole, with each other.

The frequencies at which $\varepsilon'(\nu)$ changes the sign from negative to positive, *i.e.* 278, 154, and 102 cm^{-1} for E//C, and 85 and 73 cm^{-1} for E⊥C, correspond to the longitudinal frequencies. However, it is difficult to determine all the longitudinal frequencies, because of the complex structure of the crystal and the fairly large damping at room temperature. Therefore, no further discussion will be done on the longitudinal frequencies.

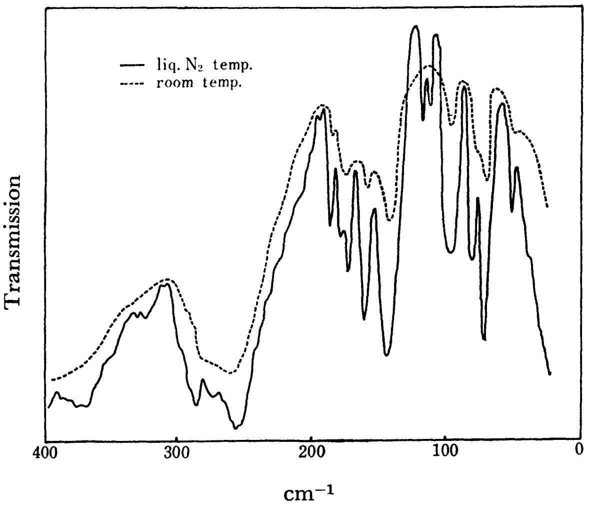

Fig. 4. Far-infrared transmission spectra of the powder sample of $CsCuCl_3$ at room and liquid-nitrogen temperatures.

Figure 4 shows the transmission spectra of the powder sample at room and liquid-nitrogen temperatures. The room temperature spectrum is essentially the same as the spectrum reported by McPherson and Chang. With lowering the temperature, the absorption bandwidth becomes narrower considerably. In the spectrum at liquid-nitrogen temperature 13 absorption bands are observed, and the vibrational assignment of each band is definitely determined as listed in Table 2, on referring to the single crystal spectra described before.

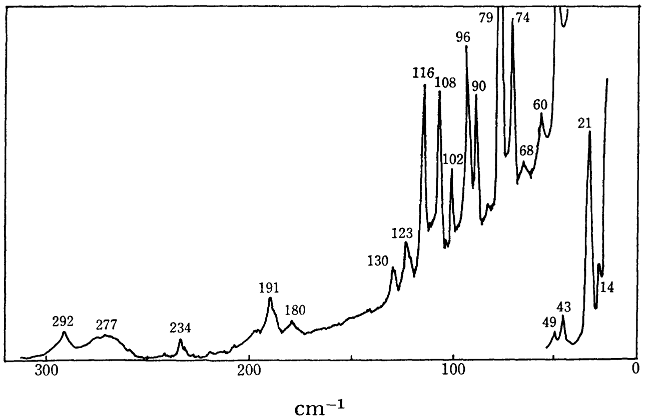

Fig. 5. Raman spectrum of the powder sample of $CsCuCl_3$ at 30 K.

The Raman spectrum of the powder sample observed at 30 K are shown in Fig. 5. Twenty Raman lines are observed, while 35 ($6A_1+14E_1+15E_2$) are expected from the factor group analysis. The E_1 modes are active both in the infrared and Raman spectra. However, a definite assignment of the Raman lines is difficult from this powder Raman spectrum only.

Spectra of the High-temperature Phase and Spectral Change Due to the Phase Transition. Figure 6 shows the far-infrared transmission spectrum of the powder sample at 175 °C. This spectrum which consists of five bands is attributable to the high-temperature phase of $CsCuCl_3$ and reveals a typical feature characteristic of the $CsNiCl_3$ type structure. The band assignment to the symmetry species is possible, on referring to the results of the polarization measurements for the $CsNiCl_3$ type crystals by Adams and Smardzewski,[9] and by the present authors.[7,10] (See Table 3.)

Figure 7 shows the far-infrared transmission spectra of the powder sample at various temperatures. The absorption bands at 52 and 39 cm^{-1} of the low-temperature phase decrease their intensities with raising temperature and disappear above 140 °C, and the new band at 42 appears in the temperature range from 140 to 150 °C. The two bands at 82 and 76 cm^{-1} in the low-temperature phase are shifted to the

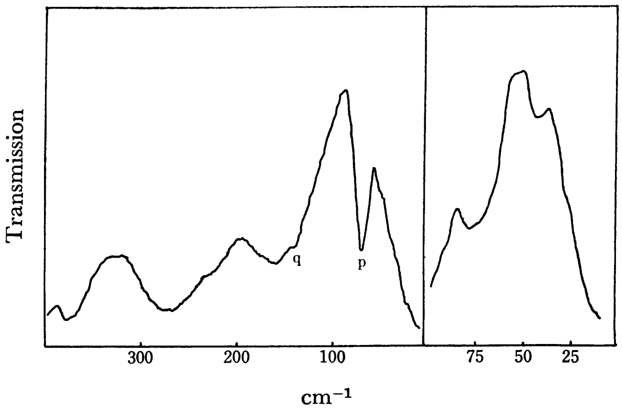

Fig. 6. Far-infrared transmission spectrum of the powder sample of $CsCuCl_3$ at 175 °C. (q and p are the absorptions by quartz and polyethylene, respectively.)

TABLE 3. VIBRATIONAL FREQUENCIES (cm^{-1}) OF THE HIGH-TEMPERATURE PHASE OF $CsCuCl_3$

270	E_{1u}
220	A_{2u}
160	E_{1u}
70	E_{1u}
42	A_{2u}

lower frequency side and merged into one at 70 cm^{-1} on transition to the high-temperature phase. The strong absorption band at 146 cm^{-1} also disappears around 140 °C and the four bands at 188, 180, 175, and 163 cm^{-1} become unresolved and are replaced by a single broad band centered at 160 cm^{-1}. The lower frequency side of the broad bands around 280—250 cm^{-1} loses its intensity, and above 140 °C only one band around 270 cm^{-1} with an unresolved shoulder around 220 cm^{-1} is observed.

Among the five bands of the high-temperature phase the 270, 220, and 160 cm^{-1} bands are rather broad, comparing with the corresponding bands of $CsNiCl_3$ crystal,[7] which is isomorphous to the high-temperature phase of $CsCuCl_3$. This fact supports the presence of a local tetragonal distortion of $CuCl_6$-octahedra suggested based on the EPR study.[3] It might be noted that the other two bands at 70 and 42 cm^{-1}, associated with the Cs^+ ion displacements, are not so broad.

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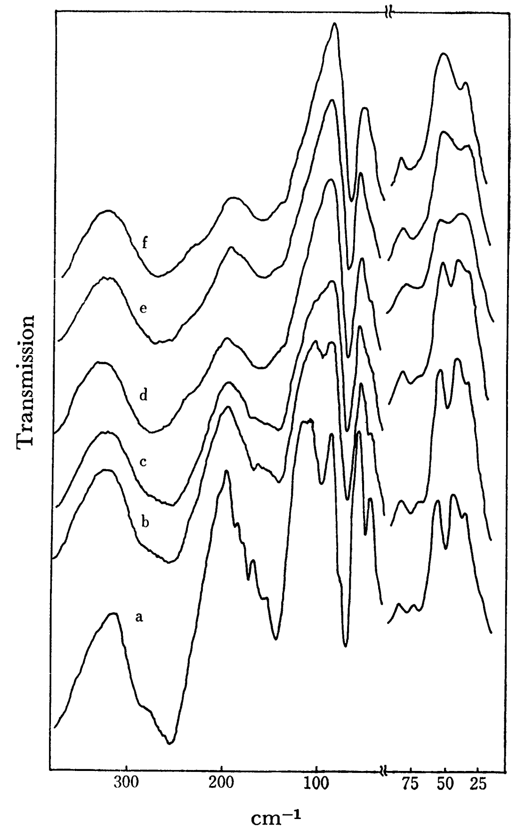

Fig. 7. Far-infrared transmission spectrum of the powder sample of $CsCuCl_3$ at various temperatures.
a: Room temperature, b: 118 °C, c: 131 °C, d: 138 °C, e: 140 °C, f: 148 °C.

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