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Abstract

Dichroic infrared (IR) absorption measurements on CN^- or OH^- centers in cadmium halide crystals were carried out at 6 K with a high spectral resolution of $0.025\,cm^{-1}$ at $2000\,cm^{-1}$, by using a FT-IR spectrometer. Several sharp absorption lines with widths less than $0.1\,cm^{-1}$ are observed in the energy region of the stretching vibration, i.e. 2000–$2250\,cm^{-1}$ for CN^- and 2500–$4500\,cm^{-1}$ for OH^-. These lines are classified into three groups attributed to: (1) an isolated center simply substituted for a halogen ion, (2) an interstitial center located between the cadmium and halogen ion sheets and (3) a coupled center with an anion vacancy. A doublet structure is observed in CdI_2 which comes from different halogen-ion sites in the 4H-polytype crystal. The isolated CN^- centers in $CdCl_2$ and $CdBr_2$ align toward Cd^{2+} ions, away from the direction of the *c*-axis. Almost all of the coupled center with a vacancy lies in a halogen-ion plane. The doublet structure of the coupled center in $CdCl_2$ and $CdBr_2$ is connected to the tunneling splitting of a vibrational level.

Keywords: CN^-; OH^-; Polarized IR absorption; Libration; Cadmium halide

1. Introduction

Cadmium halides ($CdCl_2$, $CdBr_2$ and CdI_2) crystallize in a layered structure in which a Cd^{2+} ion plane is sandwiched between two halogen-ion planes [1]. The fundamental layers stack up along the crystal *c*-axis to make up cadmium halide crystals. When doping a small amount of metal cyanide or hydroxide into these cadmium halide crystals, it is supposed that cyanide (CN^-) or hydroxyl (OH^-) ions are substituted for the halogen ions. In the present study, polarized IR absorption has been investigated on CN^- or OH^- centers doped in CdX_2 (X = Cl, Br and I) crystals. In the CdX_2 crystals, it is expected that the CN^- and OH^- electric dipoles interact with the local electric field in the crystal. A strong local electric uniaxial crystal field along the c-axis could orient the CN^- and OH^- molecular axes along that direction. This feature has not been observed in alkali-halide crystals of cubic structure [2–5].

2. Experimental procedures

The crystals were grown from melt in vacuum-sealed quartz ampules filled with $CdCl_2$, $CdBr_2$ or CdI_2 powder containing $Cd(OH)_2$ or NaCN of between 0.01 and ~2 mol% as impurities. The specimens were cleaved to a size of $10\times10\times5$–$10\times10\times12\,mm^3$ from crystal ingots. The concentration of NaCN or $Cd(OH)_2$ incorporated in the specimens was not determined in the present study. The values of concentration cited in the following are those in the melt. Crystal samples were mounted on a copper holder of a closed-cycle He refrigerator and cooled down to 6 K. The present experiments were performed at the absorption and reflection spectroscopy station on the beamline BL43IR at SPring-8, Hyogo, Japan [6]. A globar lamp (far- and mid-IR) and a tungsten lamp (mid-IR) were used as light sources. Polarized IR absorption spectra were measured over the 100–700 (far-IR) and 2000–7000 cm^{-1} (mid-IR) regions by using a wire grid polarizer for IR and a FT-IR spectrometer (Bruker IFS 120HR). The spectral resolution of this spectrometer was set to be 0.5 and 0.025 cm^{-1} at 300 and 3500 cm^{-1}, respectively.

3. Results and discussion

3.1. CN^-

Fig. 1 shows IR absorption spectra of $CdCl_2$:NaCN (2 mol%) for polarizations parallel ($E\|c$) and perpendicular ($E\perp c$) to the c-axis (E is the electric field vector of polarized light). Polarized light with $E\|c$ or $E\perp c$ was directed perpendicular to the crystal c-axis onto the polished crystal surface which includes the c-axis. The interference pattern due to BaF_2 windows of the cryostat appears in the background of both spectra. The dichroism between the $E\|c$ and $E\perp c$ spectra is remarkable. The full-width at half-maximum

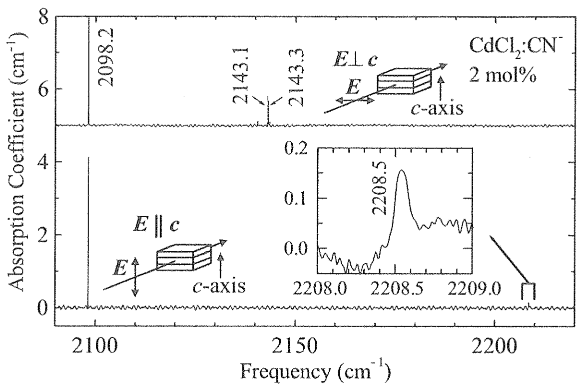

Fig. 1. IR absorption spectra of $CdCl_2$:2%NaCN measured at 6 K. The upper and lower spectra are for polarizations of $E\|c$ and $E\perp c$, respectively. The inset shows a peak due to the interstitial centers.

(0.07 cm^{-1}) of absorption lines is much narrower than those (~5 cm^{-1}) in alkali halides. The rotational motion of CN^- molecules is restrained by the local uniaxial electric field along the c-axis in the CdX_2 crystals. The local uniaxial electric field at halogen-ion sites comes from Cd^{2+} ion planes with positive charge and halogen-ion planes with negative charge.

Except for structures associated with minority isotopes, the absorption peaks are classified into three types. One type is a sharp peak at 2098.2 cm^{-1} in a lower energy region than other peaks. This peak is attributed to the stretching vibration of CN^- ions simply substituted for host halogen ions, which are called isolated CN^- centers (see Fig. 2(a)) [7,8]. It corresponds to the absorption peak due to substitutional CN^- ions for halogen ions in alkali halides [3]. This absorption peak is observed for both $E\perp c$ and $E\|c$ polarizations, which means that the dipole axis of the CN^- ion is inclined toward a Cd^{2+} ion, away from the direction of the c-axis (see Table 1). The angle θ between the dipole axis and the c-axis is estimated as

$$\theta = \tan^{-1}\sqrt{\frac{A_{E\perp c}}{A_{E\|c}}}.$$

where $A_{E\perp c}$ and $A_{E\|c}$ are areas under corresponding absorption bands in $E\perp c$ and $E\|c$ spectra, respectively.

The second type is a doublet with peaks at 2143.1 and 2143.3 cm^{-1} in the energy region higher than that of the isolated center. These absorption peaks are observed only for $\boldsymbol{E} \perp \boldsymbol{c}$ polarization suggesting that the dipole axes lie in the halogen-ion planes. These peaks may be attributed to a CN^- molecule coupled with a charge-compensated positive defect, most likely an anion vacancy, which form so-called vacancy CN^- centers (see Fig. 2(b)) [7]. When a CN^- ion combines with a vacancy through a lone-pair electron on a carbon 2s–2p hybrid orbital, the excess negative charge on the CN^- ion would decrease to make the triple bond more symmetrical and stronger, which results in the higher stretching vibrational energy [7]. The doublet structure of the coupled center in $CdCl_2$ is connected to a tunneling splitting of the vibrational level [9].

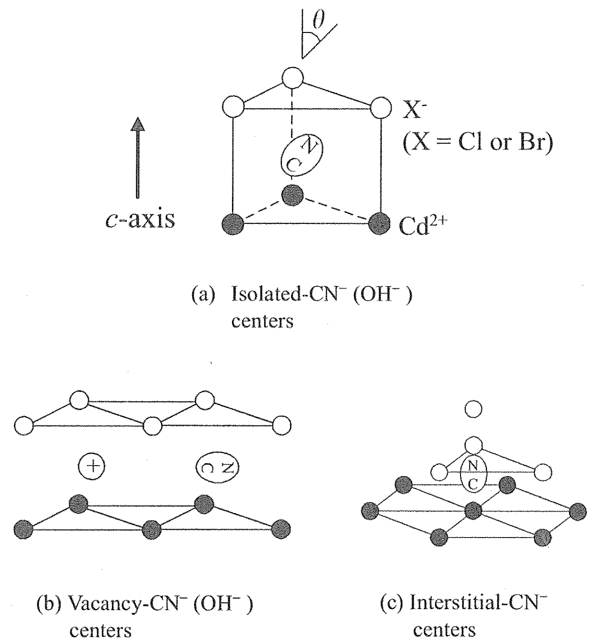

Fig. 2. Models of isolated $CN^-(OH^-)$, vacancy $CN^-(OH^-)$ and interstitial CN^- centers in CdX_2 (X = Cl, Br or I) crystals.

The third type is a peak at 2208.5 cm^{-1} in the highest energy region of these spectra. This absorption peak is observed only for $\boldsymbol{E} \| \boldsymbol{c}$ polarization. The spectral energy position, higher than that of the substitutional center, i.e. the isolated CN^- center, is proposed to come from a size effect for the CN^- center. This peak is attributed to interstitial centers in which a CN^- ion is located just above a Cd^{2+} ion and between Cd^{2+} ion and halogen-ion planes. They are called interstitial CN^- centers (see Fig. 2(c)).

Similar results are obtained in $CdBr_2$:CN^- but at somewhat lower energies (see Table 1). On the other hand, it was found that all CN^- ions doped in CdI_2 were arranged in the halogen-ion planes with their dipole axes parallel to the crystal *c*-axis, which are not shown here [8]. Each peak shows doublet structure, which is attributed to the presence of two types of I^--ion sites in the 4H polytype CdI_2 crystal [8]. The shifts of spectral positions toward the lower-energy region from

Table 1
Stretching vibrational frequencies (in cm^{-1}) and the angle θ between the dipole axis and the *c*-axis

	CN^- frequency (θ)			OH^- frequency (θ)	
Host crystal	Isolated CN^-	Interstitial CN^-	Vacancy CN^-	Isolated OH^-	Vacancy OH^-
$CdCl_2$	2098.2 (56°) [57°][a]	2208.5 (0°)	2143.1 (90°) 2143.3 (90°)	3569.6 (0°)	3885.0 (90°) 4253.2 (90°)
$CdBr_2$	2093.6 (61°) [56°][a]	2181.2 (0°)	2132.4 (73°) 2133.4 (73°)	3561.6 (0°)	3852.4 (90°) 4242.0 (90°)
CdI_2	2082.1 (0°) 2084.8 (0°) [55°][a]	2141.2 (0°) 2144.0 (0°)	[c]	3552.0[b] (0°) 3552.3[b] (0°)	3811.7 (90°) 4222.4 (90°)

[a] The angle toward the Cd^{2+}-ion from the c-axis at the halogen ion site.
[b] Estimated from the overtone spectra.
[c] Cannot be measured in absorption.

$CdCl_2$:CN^- to CdI_2:CN^- follows the size of the halogen-ion site in the host lattices whose lattice constants are $a=3.85$, 3.95 and 4.24, $c=17.46$, 18.67 and $c_{2H}=6.84$ Å for $CdCl_2$, $CdBr_2$ and CdI_2, respectively [1].

3.2. OH^-

Fig. 3 shows IR absorption spectra of $CdBr_2$:$Cd(OH)_2$ (0.1 mol%) for $E||c$ and $E\perp c$. Almost all absorption peaks are observed for the $E||c$ polarization. As described above, the CdX_2 crystals have a uniaxial crystal field in the direction along the c-axis. The dichroic absorption results show that most OH^- ions in the halogen-ion planes are arranged with their electric-dipole axes parallel to the crystal c-axis. Because the dipole moment of the OH^- ion [10] is 8 to 18 times larger than that of the CN^- ion [11], it would be energetically favorable for the OH^- electric dipoles to be aligned parallel to the direction of the c-axis.

The absorption peaks are classified into two types. A sharp main peak at 3561.6 cm^{-1} is attributed to the stretching vibration of OH^- ions simply substituted for host halogen ions, which are called isolated OH^- centers (see Fig. 2(a)). They correspond to the absorption peak due to substitutional OH^- ions for halogen ions in alkali halides [4].

The other type are peaks at 3852.4 and 4242.0 cm^{-1} in the energy region higher than that of the main band. These absorption peaks are observed only for $E\perp c$ polarization. This suggests that the dipole axes lie in halogen-ion planes. This type may be connected to an OH^- molecule coupled with an anion vacancy, which forms the so-called vacancy OH^- centers (see Fig. 2(b)). The absence of any interstitial-center mode for OH^- may be attributed to the fact that an OH^- ion combines only weakly with a Cd^{2+} ion, in contrast to the case of a CN^- ion.

A sideband associated with the main O–H stretching band was observed at 3861.2 cm^{-1}. This peak is attributed to a (stretching + libration) combination band [4,5]. The splitting energy from the main band is 299.6 cm^{-1}. The librational transition was observed directly at 300.2 cm^{-1} in $CdBr_2$:OH^- as shown in Fig. 4. The absorption edge of lattice vibrations in $CdBr_2$ is observed at 340 cm^{-1}. The direct libration band of CdI_2:OH^- is observed at 276.6 cm^{-1}, which corresponds to the splitting energy of 275.9 cm^{-1} between the main and the combination lines in CdI_2:OH^-. The direct libration of $CdCl_2$:OH^- was not distinguished owing to strong overlapping with absorption of the lattice vibrations in $CdCl_2$ (absorption edge: 480 cm^{-1}).

The vibrational sidebands have splittings slightly smaller than the frequencies of the direct

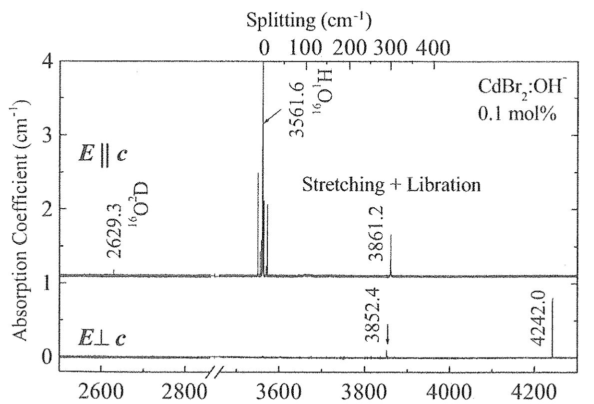

Fig. 3. The IR absorption spectra of $CdBr_2$-doped OH^- measured at 6 K. The upper and lower spectra are observed for $E||c$ and $E\perp c$ polarizations, respectively. The splitting of the combination band from the main stretching band is indicated on the upper scale.

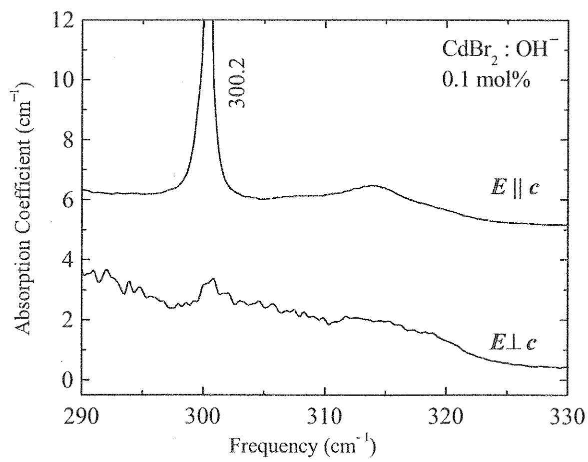

Fig. 4. The direct OH^- librational absorption band in $CdBr_2$ at 6 K. The upper and lower spectra are observed for $E||c$ and $E\perp c$ polarization, respectively.

librational bands, presumably because of the increased moment of inertia of the vibrating molecule [5]. The hydroxyl ion oscillates about its fixed center of mass, the O–H axis making an instantaneous angle θ with the c-axis. Assuming a rotational-libration potential energy of the form

$$V(\theta) = \frac{1}{2}C\theta^2,$$

then the librational frequency is given by $\omega = \sqrt{C/I}$, where $I = m_I R^2$ is the moment of inertia, $m_I = M_O M_H/(M_O + M_H)$ the reduced mass, and R is the O–H internuclear spacing. If C is assumed constant, independent of R, the increase of I would bring about a lower frequency.

4. Conclusion

In conclusion, the observed absorption structures are classified into three types, namely, isolated, interstitial and combined ones in CdX_2:Y (X = Cl, Br or I, Y = CN^- or OH^-). For the isolated type, the dipole axis (bond axis) of the CN^- ions doped in $CdCl_2$ or $CdBr_2$ incline toward Cd^{2+} ions, away from the direction of the c-axis, whereas the OH^- ions with their larger dipole moments, are arranged in the halogen-ion planes with their dipole axes parallel to the crystal c-axis. The difference between the frequencies of the direct librator and the splitting of the librational sideband can be understood in terms of the increased moment of inertia in the excited stretching-oscillational state.

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