Defect formation in layered ionic crystals of $(C_nH_{2n+1}NH_3)_2MCl_4$ (M = Cd, Cu, Mn; n = 1, 2, 3) and $CsMnCl_3 \cdot 2H_2O$

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ABSTRACT

Metal precipitation has been observed in the two dimensional crystals of alkylammonium metal chlorides, $(C_nH_{2n+1}NH_3)_2MCl_4$ which were X- or γ-irradiated at 77 K and warmed to room temperature. It has been also observed in the one dimensional crystals of $CsMnCl_3 \cdot 2H_2O$ which was irradiated at room temperature similar as photochromism of silver halides. The different temperature conditions of metal precipitation suggest a variety of defect formation mechanisms.

In alkylammonium metal chlorides, Cl_2^- molecule ions are formed at 77 K and electron trap centers are observed at 15 K with X-ray irradiation. The electron trap centers are very unstable and are bleached at temperatures higher than 30 K.

1. INTRODUCTION

It has become of interest from a new point of view to investigate atom or ion displacement induced by electron excitation in condensed materials. The ground state of crystals is the state in which variety of interaction forces are balanced. The valence electrons combine atoms or ions in crystals. When the valence electrons are excited they happen to lose the balance of the forces and then relax to new stable states in some materials. In other words, the constituent atoms or ions reconstruct the new balanced states by changing the electron state. Local structural changes are occasionally induced with the strong electron-lattice interactions.[1]

The strong electron lattice interactions create many varieties of lattice defects in alkali halides with irradiation of ultraviolet lights, X-rays and γ-rays. In this work hole trap and electron trap centers have been studied in two dimensional and one dimensional crystals. The energy of irradiated light is transformed to the momentum of ion movement through strong electron lattice interaction in these crystals.[2-4]

There are several kinds of bonds in the low dimensional crystals. The ground and the excited states are in subtle balance, thus it happens to show novel relaxation processes from the excited states of them. Alkylammonium metal halides, for instance, show the visible metal precipitation with X-rays, γ-rays and ultraviolet light (nitrogen laser) irradiation. It is interesting to investigate the influence of external stimulation of lights, in the low dimensional crystals.

Metal precipitation caused by light irradiation has been well known in silver halides as the photochromism. It occurs at room temperature (RT). It has been revealed that the silver metal precipitates with the help of impurities such as sulfur, copper and other ions in silver halides. Pure silver halide would not show the photochromism.[5] The coloration in alkali halides has been also investigated as the processes of color center formation. The typical color centers, F centers are formed at room and low temperatures. It is an essential process to create the pairs of electron trap centers and hole trap centers in the relaxation processes of excitons.

2. CRYSTAL STRUCTURES

The crystal structure of alkylammonium metal halides is similar to that of K_2NiF_4. The K, Ni and F sites are occupied by

Fig.1. Schematic representation of the part of the infinite sheet of $(C_nH_{2n+1}NH_3)_2MX_4$. Large spheres are halide anions (X^-) and small ones are metal cations (M^{2+}). Ellipsoids are alkylammonium ions.

Fig.2. The chemical unit cell of $CsMnCl_3 \cdot 2H_2O$, after Togashi *et al.* (Ref. 9)

alkylammonium ions $C_nH_{2n+1}NH_3^+$, metal cations M^{2+} and halide anions X^-, respectively.[6] A sequence of corner-sharing MX_6 octahedra form a layer structure which is sandwiched between alkylammonium layers. The NH_3^+ polar heads of alkylammonium chain point toward the layer of MX_6 and form hydrogen bonds with X^-, while the alkyl residues of the chains point away from the layer. These three-layered sheets are piled up by the van der Waals attractive force between the alkyl heads, thus these crystals are easily cleaved along the *ab*-plane (Fig. 1).
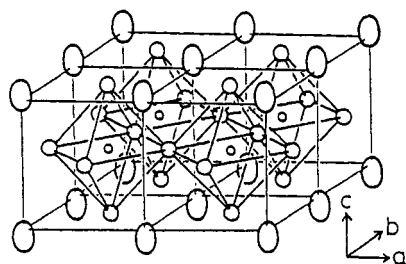
The distance between two layers of MX_6 can be modified by changing n. The ionic and spin-spin interactions between the layers of MX_6 are weaker than those of intralayers because the two layers of alkylammonium chains are inserted between the layers of MX_6 as spacers. Thus the inorganic layer of MX_6 is regarded as a two dimensional ionic crystal sandwiched by the organic layers. The family of this kind of crystals undergoes a series of structural phase transitions due to the reorientation of the alkylammonium chain. The compounds exhibit an additional transition from the paramagnetic phase to a low-dimensional ferromagnetic phase in M=Cu (n=1) and Fe, and to the antiferromagnetic phase in M=Cu (n=2,3) and Mn. The compounds of M=Cd are the diamagnetic insulators and those of M=Pb and X=I are the diamagnetic semiconductors.[7]

The structure of $CsMnCl_3 \cdot 2H_2O$ consists of the chains made of octahedra of *cis*-$MnCl_4 \cdot 2H_2O$ units bridged by single chlorine ions.[8,9] The bridging chlorine ion is puckered out along the *b*-axis in alternate fashion. Manganese cations and chlorine anions are on the zigzag lines alternately. The crystals are cleaved easily along the *ab*-plane. It is a quasi-one-dimensional antiferromagnet below the Neel temperature T_N=4.89 K. The spins of manganese cations are ordered along the *b*-axis (Fig. 2).
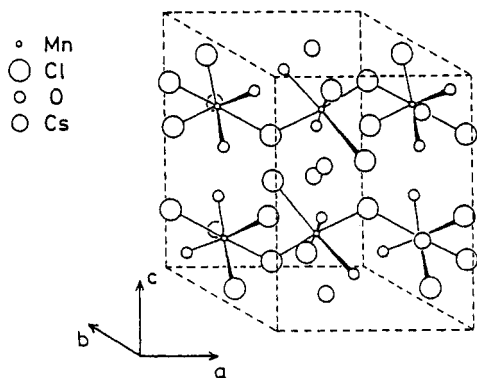
3. EXPERIMENTAL AND DISCUSSION

3.1. $(C_nH_{2n+1}NH_3)_2MCl_4$

We have investigated metal precipitation,[10,11] Cl_2^- molecule ions[12] and electron trap centers[13] in alkylammonium metal chlorides. Single crystals were obtained by evaporation of aqueous solution containing stoichiometric amounts of $C_nH_{2n+1}NH_3Cl$ (n=1,2,3) and $MnCl_2 \cdot 2H_2O$, $CdCl_2 \cdot 2\frac{1}{2}H_2O$ and $CuCl_2 \cdot 2H_2O$. The crystals were cut into platelets of about 10x10x0.5 mm³ for optical measurements. The surfaces of the platelets are parallel to the crystallographic *ab*-plane, along which the crystals are easily cleaved. The platelet mounted on the cold finger of a metal dewar was irradiated at 77 K with X-rays from the machine of a copper target operated at 40 kV and 30 mA. The crystals were also cut into the size of 3x3x10 mm³ for the electron paramagnetic resonance (EPR) measurements. They were put into the EPR glass tubes and were irradiated with Co-60 γ-rays at 77 K. The dose of the γ-rays was 6x10⁵ Gy (3x10⁴ Gy/h). A Varian E-4 EPR spectrometer and a Hitachi 330 monochromator were used for EPR and optical measurements.

3.1.1 Metal precipitation

Metal precipitation was observed in alkylammonium metal halides, $(C_nH_{2n+1}NH_3)_2MX_4$ of n=1,2,3, M=Cd,Cu,Mn and X=Cl which were irradiated with γ -rays or X-rays at 77 K. These irradiated crystals were then warmed to room temperature. At this stage we observed the irradiated areas of them show the metallic luster like a silver mirror as photographed in Fig. 3.
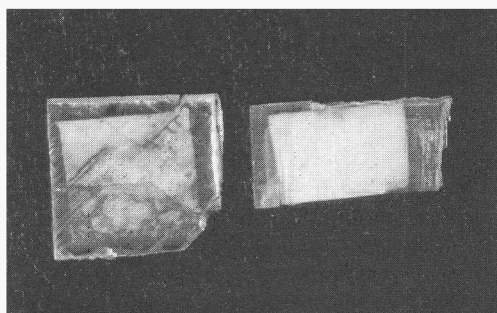
$(C_2H_5NH_3)_2CdCl_4$ $(C_2H_5NH_3)_2MnCl_4$

Fig. 3. Photographs of crystals X-irradiated at 77 K for 4 h and then warmed to room temperature. The irradiated areas exhibit metallic luster.

If the irradiated crystals are cleaved along a crystallographic *ac*-plane, the metallic luster is still observed through the newly prepared surfaces. This indicates that the metal precipitation is caused throughout the crystal irradiated with X- or γ -rays. The electrical resistance of the irradiated sample (M=Mn, n=2) was measured. The sample was warmed to room temperature after γ -ray irradiation for 70 hrs (2.1×10^6 Gy) at 77 K. The resistivity was about 5 M Ω /mm along the surface and 20 M Ω /mm between the front and the rear surfaces. Since the electrical resistance of the nonirradiated crystals were too large to be measured, its decrease was accepted as the evidence of metal precipitation. It is emphasized that the metal precipitation was not observed in the crystals irradiated at room temperature.[10]

3.1.2. Cl_2^- hole trap centers

A typical ESR spectrum of $(C_nH_{2n+1}NH_3)_2CdCl_4$ is shown in Fig. 4. The crystal was irradiated with γ -rays for 30 h at 77 K. The spectrum is complicated, but an equally spaced seven-line pattern can be distinguished from other overlapping components. The same seven-line pattern was also observed in the irradiated crystals of $(C_nH_{2n+1}NH_3)CdCl_4$ with n=2 and 3. The signal, therefore, originates from the $CdCl_6$ layer structure in these crystals. The seven lines have an intensity ratio of 1:2:3:4:3:2:1, which is very close to that of the Cl_2^- molecule ion, which is called V_k center in alkali halides. These facts suggest that the Cl_2^- centers formed in the crystals might be the origin of the ESR signal. At the bottom of the figure the signal pattern expected for the Cl_2^- is displayed as a stick diagram in consideration of two kinds of the chlorine isotopes.[11,12]

When the transparent colorless crystals of $(C_nH_{2n+1}NH_3)_2CdCl_4$ are irradiated at 77 K, the color of the crystals changes yellow. Typical optical absorption spectra are shown in Fig. 5(a) for the crystal of n=2, where the fundamental absorption tails observed before irradiation are subtracted. It is obvious that the color change is due to the main band at 26 kcm⁻¹ with the half height width of 7.5 kcm⁻¹. The unit cm⁻¹ is the inverse of the wavelength in cm unit. These values are the same as those of the V_k center (Cl_2^-) in alkali halides. It is instructive that the same kind of absorption band is observed in other cadmium compounds of n=1,3. Thus the optical transition corresponding to the main band is independent of n and the species responsible for the main band is the one produced in the layer of $CdCl_6$. Taking into account the ESR results, it is concluded that the main band is caused by the intramolecular optical transition of the Cl_2^-.
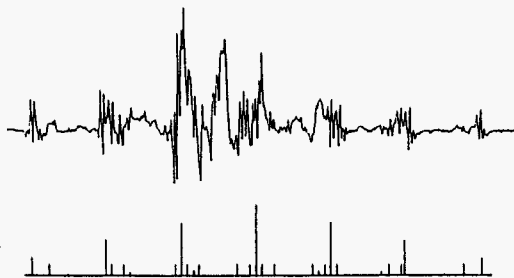

Fig.4. Second derivative ESR signal of $(C_nH_{2n+1}NH_3)_2CdCl_4$. The angle between the a-axis and the magnetic field is 35.° The seven line pattern of Cl_2^- is schematically shown by a stick diagram at the bottom of the figure.
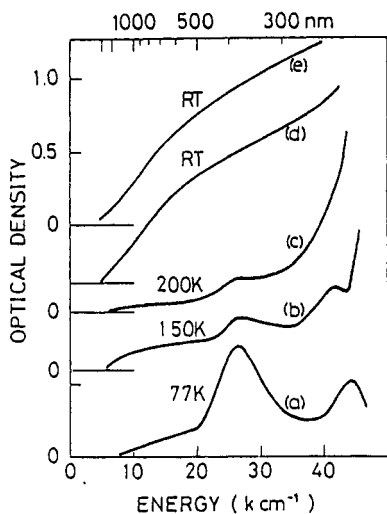
Fig. 5. Thermal behavior of the optical absorption
spectrum of $(C_2H_5NH_3)_2CdCl_4$. a: irradiated at 77 K.
b: at 150 K. c: at 200 K. d: at room temperature. e:
at room temperature after one day.

Fig. 6. The angular dependence of the hyperfine
coupling constant of the seven-line signal of
$(C_2H_5NH_3)_2CdCl_4$. The crystal was rotated around the
a-axis (a), b-axis (c) and c-axis (c).

When the irradiate crystals of M=Cd and n=1,2 were warmed
higher than 100 K, both of the optical and the ESR absorption
intensities began to decrease. The main optical absorption band
completely disappeared at room temperature and the background
absorption increased remarkably as shown in Fig. 5 (d and e). At
this stage we observed that the irradiated area of the crystal show
metallic luster like a silver mirror. This effect was also observed in
other compounds for M=Mn and Cu with n=1,2,3.

The typical angular dependence of the Cl_2^- is depicted in Figs.
6(a-c), where the data points were obtained by rotating the crystal
of n=2 around the a-, b- and c-axis, respectively. When the crystal
is rotated around the a- and b-axis, (Fig. 6(a) and (b)), the
hyperfine constants (hfc) give the maximum values of 99 G at
40,° 55,° 125° and 140.° When the crystal is rotated around the
c-axis (Fig. 6(c)), the maximum value of hfc is about 75 G which
indicates the molecular axis of Cl_2^- is deviated about 45° from the
direction of the applied magnetic field.

Fig. 7. The schematic representation of the
Cl_2^-. a: a part of the infinite layer of $CdCl_6$,
where the large and small spheres are Cl^-
and Cd^{2+}, respectively. b: two kind of Cl_2^-
which exhibited with shadowed spheres.
The type (i) is in the ab-plane and the type
(ii) is in the ac- and bc-planes.

The layer of $CdCl_6$ octahedra is illustrated in Fig, 7(a). It is possible that the two types of Cl_2^- can be formed along the
edges of the octahedra as denoted (i) and (ii) in Fig. 7(b). The type (i) is in the ab-planes and the other one (ii) is in the ac-
and/or bc-planes. When a crystal is rotated around the c-axis, the molecular axis of the type (i) is always perpendicular to
the rotating axis. As the magnetic field is applied perpendicular to the rotating axis, the molecular axis of type (i) has
chances to become parallel to the magnetic field, and in this case the hfc has the maximum value of 99 G. The maximum
value, however, is 75 G in Fig. 7(c) and the value is much smaller than 99 G. On the other hand, the type (ii) has chances
to take the maximum value of hfc, when a crystal is rotated around the a- or the b-axis as shown in Fig. 7(a) and (b). It
means that the Cl_2^- molecule axes get in parallel to the magnetic field. This is possible if the Cl_2^- molecule axes are in
the ac- and bc-planes. It is concluded from these results that the type (i) is ruled out in the compounds.
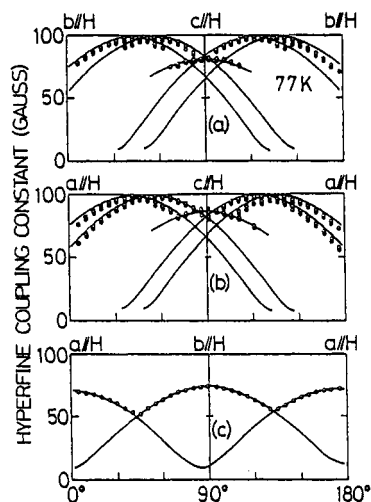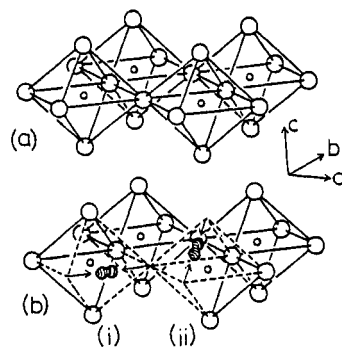
The reason why the type (ii) is preferentially created is easily speculated considering the $CdCl_6$ octahedral layers of the crystal structure. The chlorine anions are tightly bonded with metal cations in the *ab*-planes. On the other hand, the chlorine anions located on both sides of *ab*-plane are not only bonded ionically with metal cation but also bonded with hydrogens of ammonium heads by hydrogen bond. The latter bond is weaker than the former one, thus the hydrogen bonds are easily cut off with X- or γ -irradiation and the chlorine anions move to the chlorine anions on the *ab*-planes and form Cl_2^- of which axes are in the *ac*- and the *bc*-planes.

3.1.3. Electron trap centers

There occurs another question at this stage; are the electrons which were released from the chlorine anions trapped with metal cations directly and neutralize the cations or are there another steps before electrons are trapped with metal cations? We speculated that the electrons released in the early stage would be trapped primarily in shallow potential defects, and they are released from them at higher temperatures and finally captured by metal cations. If there are other electron trapping processes mentioned above, they would be observed by cooling the crystals with liquid helium. Because these traps are supposed to be shallow ones.
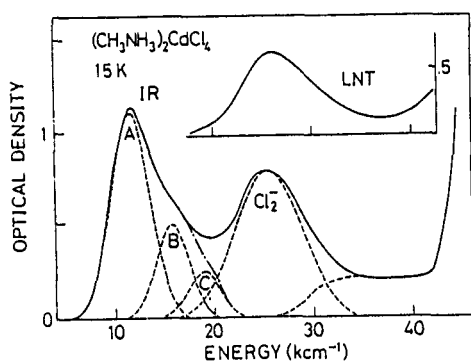

Fig. 8. Optical absorption spectrum of $(CH_3NH_3)_2CdCl_4$ X-irradiated at 15 K for 20 min. The fundamental absorption tail due to the excitonic transition at around 45 kcm^{-1} is already subtracted. The spectrum of the same compound X-irradiated at 77 K is inserted at the upper part.

Fig. 9. Optical absorption spectra of $(CH_3NH_3)_2CdCl_4$. a: X-irradiated at 15 K for 30 min. b: after 800 nm light irradiation at 15 K.

The Fig. 8 is the optical absorption spectrum (solid line) of $(CH_3NH_3)_2CdCl_4$ irradiated with X-rays for 30 min at 15 K. The X-ray machine was operated with copper target (40 kV, 30 mA). The beam direction of the X-rays was perpendicular to the *ab*-plane. An absorption band located at 25.5 kcm^{-1} with half-height width of 7.8 kcm^{-1} is identical with the absorption band observed in the crystals irradiated with X-rays at LNT. For comparison we insert the spectrum of the same compounds irradiated at LNT in the upper part of the figure. Therefore, the 25.5 kcm^{-1} band is thought to originate from the Cl_2^- molecule ion. Another absorption band (chained lines) is observed in the energy region of $8 \sim 20$ kcm^{-1}. This band could not be decomposed into two symmetric Gaussian bands, but into the three bands of A, B and C (we call them IR bands), which are illustrated with broken lines in the figure.[13] Almost the same spectrum was observed for n=2.

The IR bands are easily bleached by the light of 800 nm (12.5 kcm^{-1} at the peak energy of the A band) as exhibited in Fig. 9. At the same time about two thirds of the Cl_2^- band decreases. When the temperature of the crystals is raised higher than 30 K, the IR bands decrease and disappear almost completely at 50 K as displayed in Fig. 10. At the same stage about one third of the Cl_2^- band decreases. We suppose that the defect center, which is the origin of IR bands and is speculated to be an electron trap center, becomes unstable at temperatures higher than 30 K and the released electron recombines with the Cl_2^- center. It seems to be the most reasonable assignment that the B and C bands originate from the same ground state to different excited states, because the intensities of the B and C bands are always in proportion to the A band, and in addition, the B and the C bands are bleached by irradiation of light on the A band.
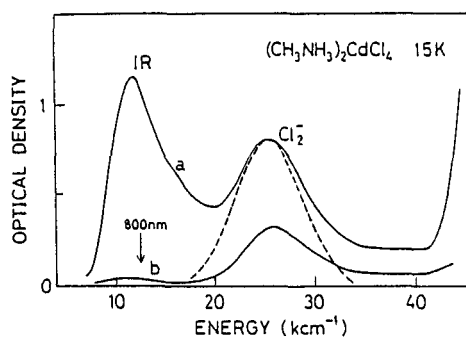
These facts mentioned above can be explained by assigning the IR bands to an electron center where an electron is trapped by an alkylammonium head in the neighborhood of a Cl^- vacancy. When the crystal is irradiated with X-rays at low temperatures, an electron is excited from the valence band composed of chlorine anions. The hole in the valence band relaxes and form a molecule ion Cl_2^-. Since the electron trap center is formed simultaneously with the Cl_2^- center, it is naturally understood by this model that the IR bands grow up in proportion to the band in the early stage of X-irradiation.

In the process of the bleaching with light, the electron trapped by the center is excited to one of the excited states and recombines probably with the nearest Cl_2^- by tunneling. Thus the bleaching of IR bands causes the decrease of Cl_2^- as seen in Fig. 9. When the irradiated cadmium compounds is bleached by 800 nm light, almost all the IR bands decrease and about
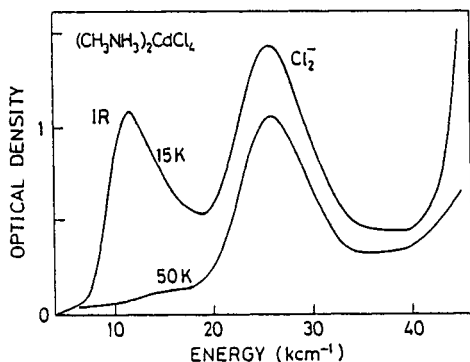

Fig. 10.   Optical absorption spectra of $(CH_3NH_3)_2CdCl_4$. a: X-irradiated at 15 K for 90 min. b: after warming to 50 K in the dark.
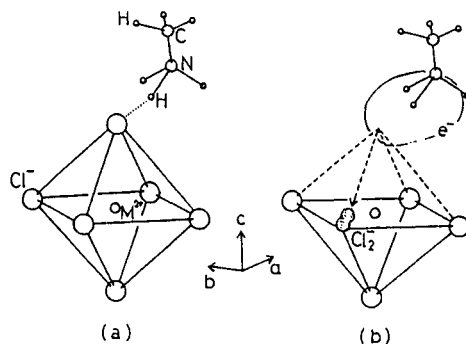

Fig. 11.   a: schematic illustration of the part of an ammonium head and a MCl_6 octahedron. b: a model of the electron trap center.

two thirds of Cl_2^- band decreases as mentioned above. On the other hand, when the irradiated crystals of cadmium compounds are warmed to 50 K, only one third of band decreases as shown in Fig. 10. The difference between the decreasing ratios may be explained as follows. When the 800 nm light is irradiated, the trapped electron is excited to its higher energy states and recombines mainly with the nearest neighbor Cl_2^- through tunneling. While, when the electron trapped centers becomes unstable thermally, the released electrons migrate through the conduction band and are trapped by metal cations which are perturbed by the nearest neighbor Cl_2^- and the energy level of which are lowered. Some of the released electrons are trapped by impurities while they are conducting through the band. Therefore, the electron released from the centers in the latter case will recombine with Cl_2^- with smaller probability than in the former case.

On the basis of the experimental evidences, we clarified that the IR bands originate from the electron trap center. The Fig. 11(a) illustrates the relative configuration of an alkylammonium head to a MCl_6 octahedron. The dotted line in the figure means a hydrogen bond between a Cl^- ion and an NH_3. The Fig. 11(b) shows schematically a molecule ion formed in the ac-plane by X-irradiation. In this case, the chlorine anion site located in the c-direction of the M^{2+} ion is vacant. As the hydrogen bond is broken, the alkylammonium head comes to have an electron affinity. Therefore, the trapped electron is thought to have a molecular orbital. If we assume that the A, B and C bands originate from the same molecular defect, they are probably assigned to the transitions from the molecular ground state to its excited states.

3.1.4. Energy band structures

The energy levels of the electron trap center are expected to lie just below the bottom of the conduction band like donor levels in semiconductors. It is important to investigate the energy band structures to know the relative configuration between the electron trap levels and the conduction bands.
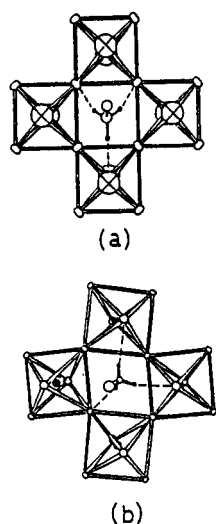
Fig. 12. Schematic representation of MX_6 octahedra and the hydrogen bonds (broken line) between the alkylammonium heads and chlorine anions, after Mokhlisse *et al*. (Ref. 14) a: orthorhombic configuration at RT. b: monoclinic configuration at 77 K.
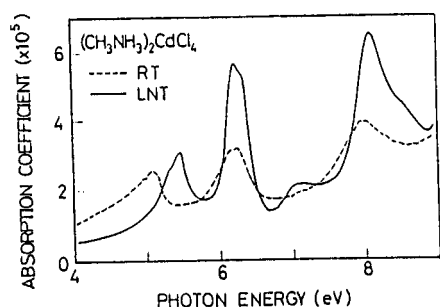

Fig. 13. Reflection spectrum. a: $(CH_3NH_3)_2CdCl_4$ at 77 K. b: $CdCl_2$ at 30 K after Pollini et al.

Fig. 14. Absorption spectra of $(CH_3NH_3)_2CdCl_4$ obtained from a Kramers-Kronig analysis of the reflectivity. a: solid line at 77 K. b: dotted line at RT.

The energy band structures are investigated by reflectivity measurements with synchrotron orbital radiation. Single crystals of cadmium compounds were cleaved along the *ab*-plane which was used as a reflection plane. The reflection spectra were measured at near normal incidence of the light to the surface of the single crystal. The light source of $3 \sim 25$ eV was the 380 MeV electron storage ring of the Synchrotron Radiation Laboratory, the Institute for Solid State Physics, the University of Tokyo. We used a monochromator of the 1 m Seya-Namioka type. The energy resolution of the spectra was about 0.025 eV at 5.5 eV. For the measurements in the energy region of $0.5 \sim 5$ eV, we used a Carl-Leiss double prism monochromator, 200 W deuteron, halogen and tungsten lamps.

Alkylammonium metal halides show a number of phase transitions due to the arrangements of the alkylammonium chains. The hydrogen bonds change drastically with the crystal temperature as shown in Fig. 12. Thus the relative arrangement between hydrogen atoms and chlorine anions at RT is very different from that at LNT. On the other hand, the arrangement between the metal cation and six chlorine anions around it hardly changes.[14]

The $CdCl_2$ crystal is a suitable reference compound to determine the energy band structure of the present materials. The energy band structure of it was investigated by Pollini *et al.*[15] The top of the valence band is composed of Cl $3p$ and the bottom of the conduction band is composed of Cd $5s$. From the structural similarity between the cadmium chloride layers of $CdCl_2$ and $(C_nH_{2n+1}NH_3)_2CdCl_4$, it is supposed that the latter compounds have energy band structures similar to those of the former ones.

The reflection spectrum of $(CH_3NH_3)_2CdCl_4$ is shown in Fig. 13(a). The spectral profile is quite similar to that of $CdCl_2$ (Fig. 13(b)) except for the lowest energy peak at 5.48 eV (LNT), which is characteristic of the present compounds.[16] The absorption spectra obtained from the reflectivity by a Kramers-Kronig analysis are shown in Fig. 14. In the calculation, the reflectivity in the energy region higher than 25 eV was extrapolated with a damping factor of E^{-4}.
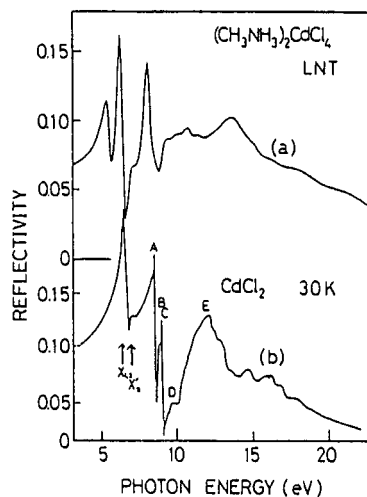
The lowest energy peak at 5.48 eV (LNT) is the newly observed one. The next peak at around 6.2 eV is the one which corresponds to the electronic transition from the Cl $3p$ valence band to the Cd $5s$ conduction band of $CdCl_2$. These two bands have comparable intensities and doublet structures of the same order of 0.1 eV. However, the lowest peak at 5.48 eV shifted by 0.38 eV to the lower energy region as the crystal was warmed to RT, while the peak at around 6.2 eV shifted by only 0.1 eV. The splitting of the doublet structures is nearly equal to the spin-orbit splitting of a chlorine atom. Therefore, the Cl $3p$ valence band are attributed to the transitions from the same initial state of the Cl $3p$ valence band to the two different kinds of conduction bands. One is the conduction band composed of Cd $5s$ which corresponds to that consisting of $CdCl_2$. The other is a new type of conduction band composed of alkylammonium heads, because the NH_3^+ heads are also able to accept electrons from chlorine ions; the NH_3^+ heads form another kind of conduction band. The energy shift of the latter type band is thought to be much larger than that of the former one, because relative arrangement of the NH_3^+ heads to the chlorine ions changes drastically between RT and LNT as seen in Fig. 12, while relative arrangement of the chlorine ions to the metal cation in the $CdCl_6$ octahedron does not change so much. As mentioned above, the observed temperature dependence of the absorption peak seems to support our proposal for the electronic transition. In conclusion, the lowest energy peak at 5.48 eV is thought to be the electronic transition from the Cl $3p$ valence band to the conduction band composed of the NH_3^+ heads. The new type of exciton band is also observed in the other cadmium chloride compounds with n=2 and 3.

3.1.5. Mechanism of metal precipitation

Taking into account the experimental results mentioned above, the crystal structure near the electron trap center of ammonium head is deformed by cutting off the hydrogen bonds, thus the ground state of the electron trap center is just below the conduction band composed of NH_3^+ heads. When the crystal is warmed higher than 30 K, the electrons clear the small energy barrier with the thermal energy and they are released to the conduction band. The electrons migrate through the conduction band and only one-third of them are trapped with Cl_2^- and recombine with them. Two-thirds of the released electrons neutralize the cadmium cations Cd^{2+} partly as exhibited in Fig. 10. On the contrary, when the electron trap center is irradiated by the light (800 nm), the trapped electron is excited to the higher energy state which lies just below the Cd^{2+} conduction band and above the ammonium conduction band. The wavefunction of the excited electron is large, hence the electrons mainly tunnel to the Cl_2^- and reduce more than half of them as seen in Fig. 9.

The energy level of Cl_2^- is just above the valence band which is composed of chlorine anions, because it is the hole trap center. The Cl_2^- becomes unstable at higher temperatures than 100 K, and the chlorine molecules, Cl_2 are ejected from the crystals.[10] The electrons left in this process are transferred to the partly neutralized metal cations (M^+) and neutralize them. These neutralized metal atoms (M) migrate in the crystal and coagulate and form metal colloids. The sizes of these metal colloids distribute from the small sizes to the large sizes of several microns order. Each of them scatter the incident light of which wavelengths are the same as the sizes of them, thus the absorption spectra are those of Fig. 5(d) and (e). This is known as the Mie scattering.

3.2. $CsMnCl_3 \cdot 2H_2O$

Metal precipitation has been also observed in $CsMnCl_3 \cdot 2H_2O$ which were irradiated with X-rays or γ-rays. (Fig. 15) The conditions of the metal precipitation in this substance are quite different from those in $(C_nH_{2n+1}NH_3)_2MCl_4$. The metal precipitation occurs in $CsMnCl_3 \cdot 2H_2O$ only when it is irradiated at RT, and was not observed when it was irradiated at LNT. The differential spectrum is shown in Fig. 16 which is the difference between the spectra of the virgin crystal
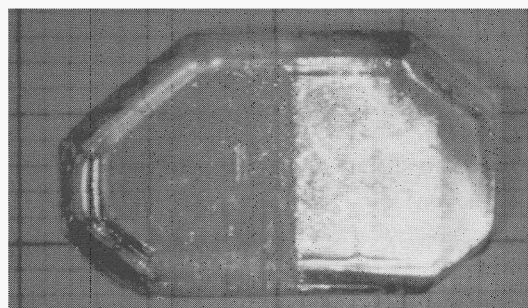

Fig. 15. The photograph of $CsMnCl_3 \cdot 2H_2O$ X-irradiated at RT. The left half was covered with lead plate and was not irradiated with X-rays.
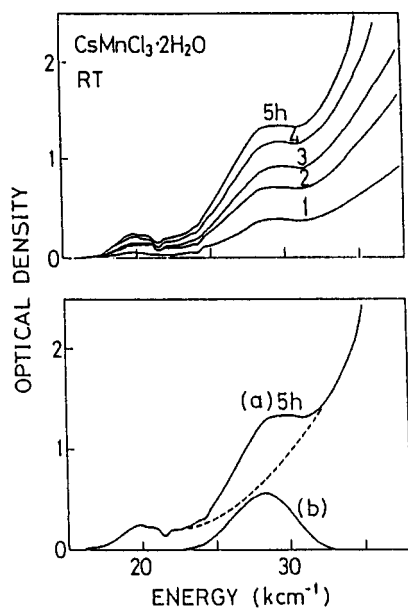
Fig. 16. The Differential optical absorption spectra of $CsMnCl_3 \cdot 2H_2O$ irradiated with X-rays at RT.

and of the irradiated one. An absorption band increases in the energy region of $23 \sim 32$ kcm^{-1} which is not exactly the same as that of Cl_2^- but similar to that. Thus some kinds of hole centers are supposed to be formed in $CsMnCl_3 \cdot 2H_2O$. The similar absorption spectra were also observed when the crystals were irradiated with γ-rays at LNT. From the experimental results mentioned above, the hole trap centers are effective at RT but not effective at LNT for the metal precipitation, if they have some roles for it. The reason is not clear yet but is speculated that the small size of metal colloids are also formed at LNT as they are formed at RT, but they are very small and do not migrate because the thermal energy is not enough to migrate for them at LNT. On the contrary, small metal colloids migrate and form large colloids when the compound is irradiated at RT.

Acknowledgments

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