

Infrared absorption study of $\text{Cr}(\text{CN})_6^{n-}$ complexes doped in KCl crystals

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Abstract. Infrared absorption spectrum of $\text{Cr}(\text{CN})_6^{3-}$ doped in KCl crystals show that the site symmetry of the ion is predominantly C_2 corresponding to one cation vacancy in the nearest neighbour and the other in the next nearest neighbour position with respect to Cr^{3+} ion. X-irradiation produces complexes of the type $\text{Cr}(\text{CN})_6^{4-}$ and $\text{Cr}(\text{CN})_6^{5-}$.

Keywords. Infrared absorption; crystal field symmetry.

1. Introduction

The infrared absorption spectra of molecular ions doped in alkali halide crystals have drawn considerable attention recently (Jain *et al* 1971). The infrared absorption spectra give information about the site symmetry of the ion (Decius *et al* 1963), the nature of the impurity-host lattice interaction (Metselaar and Van der Elksen 1968), etc. It has been shown (Jain *et al* 1972) that the charge state of the cyano complexes doped in alkali halide crystals can be changed by x-irradiation. In these complexes the $C \equiv N$ stretching frequency changes when the charge state of the central metal ion is changed (Nakamoto 1970). In addition, the infrared absorption shows structure in the $C \equiv N$ stretching region depending upon the site symmetry of the complex. In this paper we report the results obtained on the infrared absorption from $\text{Cr}(\text{CN})_6^{3-}$ complex doped in KCl crystals.

Experimental

KCl crystals containing $\text{Cr}(\text{CN})_6^{3-}$ were grown by slow evaporation of the saturated solution of analar grade KCl containing known amount of $\text{K}_3\text{Cr}(\text{CN})_6$. By this method crystals of size $5 \text{ mm} \times 5 \text{ mm} \times 2 \text{ mm}$ could be easily obtained.

The concentration of $\text{Cr}(\text{CN})_6^{3-}$ present in the crystal was determined by dissolving a known weight of crystal in known quantity of distilled water and measuring the peak height of 3778 \AA band in the solution. The concentration of $\text{Cr}(\text{CN})_6^{3-}$ corresponding to this band height was read from the calibration curve obtained by measuring the optical density of the 3778 \AA peak as a function of concentration of $\text{K}_3\text{Cr}(\text{CN})_6$ in water solution.

The infrared absorption spectrum was recorded using a Carl Zeiss U.R. 20 infrared spectrophotometer. Spectra were recorded at room temperature as

well as low temperature. For low temperature measurement a cryodyne cooler made by Cryogenic Technology, Inc., USA, was used. The crystals were x-irradiated at room temperature by keeping them at the window of a Rich Zeibert x-ray machine with Fe target-operating at 25 KV and 7 mA.

3. Results

Figure 1 (a, b) shows the infrared absorption spectrum observed in KCl : $\text{Cr}(\text{CN})_6^{3-}$ crystals at room temperature and 32° K respectively. Figure 1 (c, d, e) are the spectra for crystals x-irradiated for different times at room temperature and figure 1 (f) is the low temperature (30° K) spectrum of the 8 hrs x-irradiated crystal. The peak positions of the absorption bands before and after x-irradiation are given in table 1.

4. Discussion

4.1. Symmetry of the ion

$\text{Cr}(\text{CN})_6^{3-}$ belongs to the point group O_h . It occupies 7 lattice sites in KCl lattice, substituting one K^+ site by Cr^{3+} and six Cl^- sites by six CN^- ions similar to $\text{Co}(\text{CN})_6^{3-}$ (Jain *et al* 1972) and $\text{Fe}(\text{CN})_6^{3-}$ (Jain *et al* 1973) in alkali halide crystals. Thus in the absence of any defects in the neighbourhood, the site symmetry of $\text{Cr}(\text{CN})_6^{3-}$ ion in the lattice should be O_h .

Since Cr ion is in the trivalent state, the two extra positive charges of each ion

Table 1. Assignment of observed infrared absorption peaks in as grown and x-irradiated KCl: $\text{Cr}(\text{CN})_6$ crystals

As grown		X-irradiated		Assignment	Molecular species
RT	Low temperature	RT	Low temperature		
	2123 cm^{-1} (W)		2135 (VW)	$\nu_1 (C_g)$] $\text{Cr}(\text{CN})_6^{3-}$
	2132 cm^{-1} (W)		2132 (VW)	$\nu_3 (C_g)$	
2123 cm^{-1} (S)	2123 cm^{-1} (S)	2124 (M)	2124 (M)	$\nu_6 (C_g)$	
2118 cm^{-1} (VS)	2119 cm^{-1} (S)	2118 cm^{-1} (M)	2119 (M)] CN^-
		2100 (M)	2102 (M) 2070		
		2068 (M)	2080 (M)	?	
		2045 (S)	2044 (S) 2046	$\nu_6 (C_{2v})$	
		2037 (S)	2036 (M)		$\text{Cr}(\text{CN})_6^{4-}$
		2018 (VS)	2016 (VS)		
		1922 (VS)	1918 (VS)	$\nu_6 (O_h)$	$\text{Cr}(\text{CN})_6^{5-}$

has to be compensated either by a trivalent anion impurity or by two cation vacancies. These cation vacancies can be in the nearest or next nearest neighbour cation positions of the complex with almost equal probability (Tosi and Airoldi 1958, Watkins 1959). The presence of these vacancies lower the O_h symmetry of the complex. Since two cation vacancies repel each other, those configurations in which they lie near each other are not favoured. Thus the vacancies can be either both along $\langle 110 \rangle$ giving rise to D_{2h} site symmetry or one vacancy along $\langle 110 \rangle$ and the other along $\langle 100 \rangle$ on either side of the metal ion giving rise to C_s symmetry. If, on the other hand, both the vacancies occupy next nearest neighbour position, the symmetry becomes D_{4h} .

In octahedral symmetry O_h , only one $C \equiv N$ stretching mode $\nu_6 (T_{1u})$ is allowed in infrared. On lowering the symmetry to D_{2h} , ν_6 splits into three (B_{1u} , B_{2u} , B_{3u}). For C_s symmetry $\nu_6 (T_{1u})$ splits into $2A' + A''$ (Wilson *et al* 1955). In addition, $\nu_1 (A_{1g})$ and $\nu_3 (E_g)$ modes, which are only Raman active in O_h , become infrared active in C_s symmetry. If the symmetry of the complex is D_{4h} , $\nu_6 (T_{1u})$ will split into two (A_{2u} , E_u) and $\nu_1 (A_{1g})$ and $\nu_3 (E_g)$ still remain infrared inactive. Thus from the observed infrared spectrum one can identify the site symmetry of the ion in the host lattice and hence the position of the vacancies.

4.2. Unirradiated crystals

In the infrared absorption spectrum we observe one very strong band at 2119 cm^{-1} and another band at 2124 cm^{-1} having a shoulder on the high energy side. The intensity of the 2119 cm^{-1} band is nearly double that of 2124 cm^{-1} band. On cooling the crystal to 32° K , 2119 cm^{-1} band broadens into an overlapping doublet and height approaches that of 2124 cm^{-1} . The shoulder on the high energy side resolves into two weak bands at 2131 cm^{-1} and 2135 cm^{-1} .

Since our spectrum (on cooling) shows almost three equally strong peaks and two weak bands the site symmetry of the ion is predominantly C_s . The two weak bands at 2135 and 2132 cm^{-1} that appear clearly at low temperature are assigned to the infrared inactive $\nu_1 (A_{1g})$ and $\nu_3 (E_g)$ modes becoming active in C_s symmetry and the strong band at 2124 and the doublet at 2119 cm^{-1} to ν_6 mode. Caglioti *et al* (1958) have reported $\nu_1 (A_{1g})$ at 2137 and $\nu_3 (E_g)$ at 2063 cm^{-1} . We do not observe any band below 2118 cm^{-1} in unirradiated crystal. Thus the peak positions given by Caglioti *et al* for $\nu_3 (E_g)$ seem to be in error. On comparing the position of ν_3 band with other hexacyanide complexes it would appear that this band should have a frequency in between ν_1 and ν_6 .

4.3. X-irradiated crystals

On x-irradiation new strong and sharp bands appear on the low energy side of the bands due to $\text{Cr}(\text{CN})_6^{3-}$ and the bands in the unirradiated crystal decrease in intensity as shown in figure 1 (c)-1 (e). Irradiation for one hour produces only bands around 2030 cm^{-1} . On prolonged irradiation these bands become very strong and additional weak bands appear at 2100 , 2070 cm^{-1} with a very strong band at 1920 cm^{-1} . When the irradiated crystal is cooled to 32° K these bands become sharp and well resolved as shown in figure 1 (f).

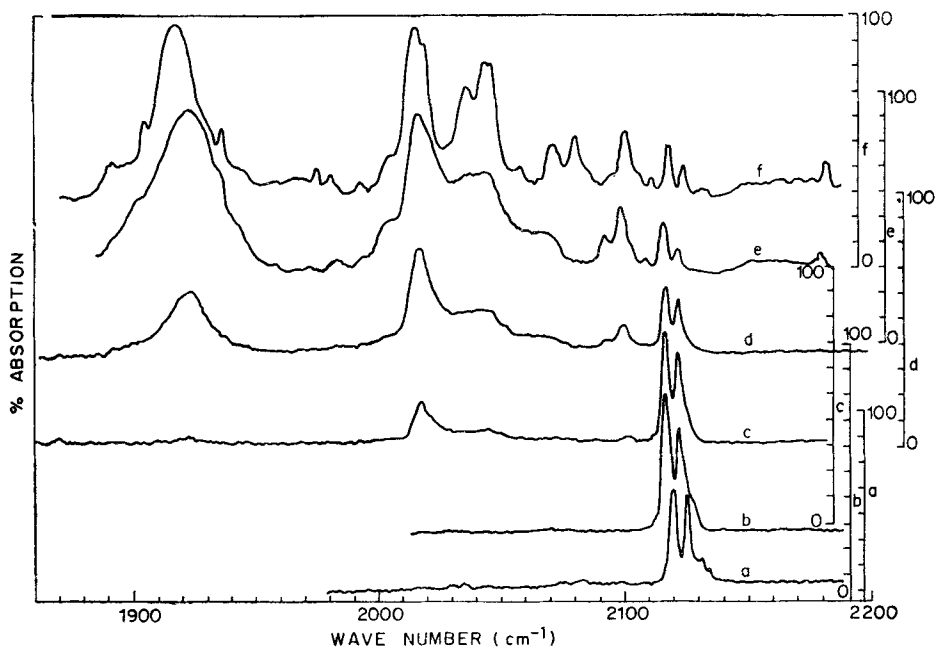


Figure 1. Infrared absorption spectrum of $\text{Cr}(\text{CN})_6^{3-}$ doped in KCl crystals.

- (a) as grown crystal at 32°K (0.3%).
 (b) as grown crystal at room temperature (0.3%).
 (c) 1 hour x-irradiated crystal (0.5%).
 (d) 2 hours x-irradiated crystal (0.5%).
 (e) 8 hours x-irradiated crystal at room temperature (0.3%).
 (f) 8 hours x-irradiated crystal at 33°K (0.3%).

It has been shown (Jain *et al* 1972, 1973; Nakamoto 1970) that the $C \equiv N$ stretching frequency of cyano complexes of a metal changes with its charge state. Vibrational frequency decreases with decrease in the charge state of the central metal ion. Thus we expect that the lower energy absorption bands which appear on irradiation are due to those $\text{Cr}(\text{CN})_6$ complexes in which Cr ion is in divalent or monovalent states. On x-irradiation, the electrons released by Cl^- are captured by the complex and converted into $\text{Cr}(\text{CN})_6^{4-}$ and $\text{Cr}(\text{CN})_6^{5-}$ i.e., the trivalent Cr^{3+} ions is converted into divalent and monovalent respectively.

We assign the absorption bands around 2030 cm^{-1} to $\text{Cr}(\text{CN})_6^{4-}$ complex and the strong absorption band at 1920 cm^{-1} to $\text{Cr}(\text{CN})_6^{5-}$ complex formed on x-irradiation.

For $\text{Cr}(\text{CN})_6^{4-}$ complex, Cr ion being in divalent state, only one cation vacancy will be needed for charge compensation. Depending upon whether the cation vacancy occupies the nearest neighbour position or the next nearest position the site symmetry of the complex will be C_{2v} or C_{4v} respectively. In C_{2v} symmetry ν_6 splits into three components A_1 , B_1 and B_2 and ν_1 (A_{1g}) and ν_3 (E_g) become infrared active, whereas in C_{4v} symmetry ν_6 splits into two components A_1 and E and ν_1 (A_{1g}) and ν_3 (E_g) become infrared active. In the x-irradiated crystal we can see three well resolved bands around 2020 cm^{-1} region at low temperature. In addition there are two weak bands on the higher energy side. This shows that the site symmetry of $\text{Cr}(\text{CN})_6^{4-}$ complex is predominantly C_{2v} . This is

expected since the vacancy in the next nearest neighbour position (around $\text{Cr}(\text{CN})_6^{3-}$) can migrate away easily during irradiation.

Since Cr is in monovalent state in $\text{Cr}(\text{CN})_6^{5-}$, there need not be any charge compensating vacancy and the symmetry of the complex should be perfectly O_h , giving rise to a single absorption band in the infrared. The spectrum shows a single strong band at 1922 cm^{-1} as shown in figure 1 (e). We assign this to $\text{Cr}(\text{CN})_6^{5-}$ complex.

In the case of $\text{Cr}(\text{CN})_6^{3-}$, doped in KCl, on x-irradiation, the electrons captured by the Cr ions go into the $d\epsilon$ orbital. Thus the d electron configuration changes from d^3 to d^4 and d^5 when the charge state is changed to divalent or monovalent respectively. Therefore, one would expect the $C \equiv N$ stretching band corresponding to these complexes to be very intense compared to the trivalent complex (Jones 1971). Indeed the intensity of the bands assigned to $\text{Cr}(\text{CN})_6^{4-}$ and $\text{Cr}(\text{CN})_6^{5-}$ are at least ten times those corresponding to $\text{Cr}(\text{CN})_6^{3-}$, thus supporting our interpretation.

The weak bands that appear around 2100 cm^{-1} on prolonged irradiation may be due to the formation of CN^- ions. The other new weak peaks that appear could be due to new complexes of $\text{Cr}(\text{CN})_6$ in which one or two of the CN^- ions are knocked off. At the present stage we cannot give an unambiguous assignment for these bands.

Conclusion

Infrared absorption spectrum of $\text{KCl} : \text{Cr}(\text{CN})_6^{3-}$ crystals show that the trivalent complex is predominantly in C_4 symmetry. x-irradiation produces tetravalent and pentavalent $\text{Cr}(\text{CN})_6$ complexes in which Cr is in divalent (d^4) and monovalent (d^5) state respectively.

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