Evidence for 'C' Terms in the Magnetic Circular Dichroism of $Fe(CN)_6^{3-}$

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Summary An investigation of the magnetic circular dichroism of ferricyanide ion doped into two host lattices shows that the spectra obey the $1/T$ law expected from Faraday C terms down to 12 K; this contradicts a previous study of the ion dissolved in a PVA glass.

THE interpretation of the charge transfer absorption spectrum of $Fe(CN)_6^{3-}$ as revealed by magnetic circular dichroism[1] (m.c.d.) rests heavily on the assumption that the m.c.d. spectrum consists mainly of Faraday C terms.[2]

The bands in question are due to L → M charge-transfer transitions and are identified as ${}^2T_{2g} \rightarrow {}^2T_{1u}(\pi)$, $\rightarrow {}^2T_{2u}(\pi)$, and $\rightarrow {}^2T_{1u}(\sigma)$ at 24,500, 32,700, and 40,500 cm^{-1} respectively on the basis of comparison of calculated C/D values with those obtained experimentally. Thus a rough symmetry calculation gave[1] $C/D = -0{\cdot}5$, $+0{\cdot}5$, and $-0{\cdot}5\ \beta$ for these three transitions respectively compared with $-0{\cdot}64$, $+0{\cdot}69$, and $-0{\cdot}87\ \beta$ obtained experimentally from a room temperature solution measurement. Crude heating experiments[3] indicated approximate $1/T$ behaviour.

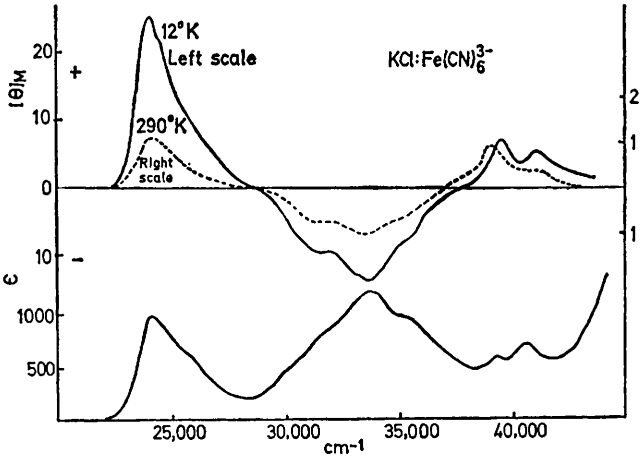
	Band I (24,500 cm^{-1})				Band II (32,700 cm^{-1})			
Temperature/K	$B + C/kT$ ($d^2\ \beta$ cm^{-1})/10^{-3}	C^a ($d^2\ \beta$)	D (d^2)	C/D^a (β)	$B + C/kT$ ($d^2\ \beta$ cm^{-1})/10^{-3}	C^a ($d^2\ \beta$)	D (d^2)	C/D^a (β)
290	$-3{\cdot}87$	0·66	1·54	0·43	$+4{\cdot}54$	0·77	2·87	0·27
12	$-76{\cdot}1$	0·53	1·61	0·332	$+55{\cdot}8$	0·43	3·00	0·131

[a] Assuming B = 0.

Kobayashi *et al.*[4] measured the m.c.d. of $Fe(CN)_6^{3-}$ down to 77 K and found that the measured $[\theta]_m$ did not obey the $1/T$ law expected for pure C terms.

We present evidence to show that the charge-transfer bands in $Fe(CN)_6^{3-}$ obey the $1/T$ law down to liquid helium temperatures.

We have measured the m.c.d. and absorption spectra of $Fe(CN)_6^{3-}$ at room temperature and at 12 K in two matrices. First we have doped the ion into KCl where it substitutionally replaces the entity KCl_6^{5-}. This isotropic host lattice shows no strain or compression effects in the electronic spectra of the ferricyanide ion and can be taken down to low temperatures without sustaining damage. Secondly we have introduced the n-butylammonium salt of $Fe(CN)_6^{3-}$ into a rigid matrix of polymethyl methacrylate which also may be taken safely to helium temperatures. The latter sample was heated a few degrees at low temperature to demonstrate the temperature dependence. The KCl–$Fe(CN)_6^{3-}$ sample shows good $1/T$ behaviour for 300 and 12 K and gives no evidence for dominant B term character. The C/D values at the two temperatures are given in the Table and it is clear that the m.c.d. bands are mostly C term in character as assumed in the original interpretation.[1] The results in the rigid polymethyl methacrylate polymer



The m.c.d. and absorption spectra of ferricyanide ion doped into KCl. *ε is the molar extinction coefficient for the* 12 *K absorption spectrum* (*lower curve*); $[\theta]_m$ *is in deg dl dm*$^{-1}$ *mol*$^{-1}$ *per gauss.*

matrix also show the same $1/T$ dependence down to 12 K and in the heating experiments at low temperature.

It is clear, therefore, that the original interpretation of the ferricyanide m.c.d. spectra as due to C terms was justified and that there is little B term contribution. The spectra in the host lattices we have used show that angular momentum is not quenched by any intramolecular process. Thus the discovery of reduced C/D in the PVA films cannot be due to covalence or to vibronic interactions (as opposed to electron-lattice interactions) and their interpretations must be rejected. Our evidence clearly points to distorting effects from the host medium. Reduction of symmetry induced by the host lattice would cause quenching of the angular momentum. If this process is responsible for the PVA results an upper limit of 100—200 cm^{-1} may be placed upon the distortion since the full solution C/D values are recovered at room temperature. Another possibility exists for lack of $1/T$ behaviour in polymer matrices, namely that the samples are not actually at the temperatures expected. The polymers are often poor conductors of heat and local heating may be introduced by the light beam in the region of the absorption band and by radiation from room temperature windows. This may be prevented by efficient thermal contact to the cryostat and by the use of transparent low temperature radiation shields.

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