Aftereffects of the Cobalt-57–Iron-57 Electron-capture Reaction in Cobalt-57-doped Tricadmium Bis[hexacyanoferrate(III)] Dodecahydrate

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Mössbauer-emission spectra of cobalt-57-doped $Cd_3[Fe(CN)_6]_2,12H_2O$ have been recorded at various temperatures and resolved into two doublets, one symmetric for the parent $[Fe(CN)_6]^{3-}$ and one asymmetric attributed to a square-pyradimal $[Fe(CN)_5]^{2-}$ complex. The asymmetry vanishes with increasing temperature and thus cannot be attributed to a Goldanskii–Karyagin effect. The possibilities of paramagnetic relaxation are briefly discussed.

MÖSSBAUER spectra of sources containing the $[^{57}Co(CN)_6]^{3-}$ complex have not only a doublet corresponding to $[^{57}Fe(CN)_6]^{3-}$, but also a doublet which we have attributed to $[^{57}Fe(CN)_5]^{2-}$; apparently the Auger charging following the ^{57}Co–^{57}Fe electron-capture decay can cause fragmentation of a newly formed ^{57}Fe hexacyanide.[1] In a recent paper [2] we showed that the intensity of the source spectrum of $Cd_3[^{57}Co(CN)_6]_2,12H_2O$ decreased more rapidly with temperature than one would expect from the temperature dependence of absorber spectra of $Cd_3[Fe(CN)_6]_2,12H_2O$. This indicates that the proposed $[^{57}Fe(CN)_5]^{2-}$ complex is more loosely bound in the lattice than the $[^{57}Fe(CN)_6]^{3-}$ complex; the corresponding Debye temperatures were estimated to be *ca.* 170 and 230 K respectively.

The interpretation [2] of our experimental results was not entirely satisfactory. (*i*) At low temperatures the source spectra could not be accounted for by two symmetric doublets; we introduced a third doublet, but were not able to identify it satisfactorily. (*ii*) It was necessary to assume that the relative yield of the $[^{57}Fe(CN)_5]^{2-}$ increases with temperature, possibly due to temperature-dependent diffusion of a decoupled CN^- ligand. (*iii*) The temperature dependence of the quadrupole splitting of the alleged $[Fe(CN)_5]^{2-}$ was similar to that of $[Fe(CN)_6]^{3-}$; this is surprising, since for substituted pentacyanides the quadrupole splitting is almost entirely generated by asymmetric covalent bonding and normally independent of temperature.

In order to elucidate these points we have repeated the investigation on ^{57}Co-doped $Cd_3[Fe(CN)_6]_2,12H_2O$. Since cobalt and iron hexacyanides form isomorphic crystals,[3] $[^{57}Co(CN)_6]^{3-}$ can easily be introduced at $[Fe(CN)_6]^{3-}$ sites; in this way we can exclude the possibility that the ^{57}Fe-labelled species have their f factors changed merely by their sitting in a ' cobalt ' lattice. Further we have described the spectra assuming an asymmetric doublet for the alleged $[^{57}Fe(CN)_5]^{2-}$. Such asymmetry can, as reviewed by Greenwood and Gibb,[4] have various causes; for the $[^{57}Fe(CN)_5]^{2-}$ complex two of these appear possible, anisotropy of the recoil-free fraction (the so-called Goldanskii–Karyagin effect) and electronic spin relaxation.

Pentacyanoferrate(III), formed by the abstraction of a CN^- ligand from hexacyanoferrate(III), must be square pyramidal with a symmetric electric-field gradient around the central axis. If the mean-square amplitude of vibration of iron in $[Fe(CN)_5]^{2-}$ is anisotropic, it probably has its highest value in the direction of the ligand vacancy. Therefore, in the case of a Goldanskii–Karyagin effect, the $(\pm 3/2 \rightarrow \pm 1/2)$ transition corresponds on average to emission in a direction with lower f factor than does the $(\pm 1/2 \rightarrow \pm 1/2)$ transition. The $(\pm 3/2 \rightarrow \pm 1/2)$ line will consequently be weakest. Since the f factor is related to the mean-square amplitude by $f = \exp(-\text{constant}\ \langle x^2 \rangle)$ (see ref. 4), the asymmetry of the quadrupole doublet must increase with increasing temperature.

By analogy with $[Co(CN)_5]^{3-}$, formed in electron-irradiated $K_3[Co(CN)_6]$,[5] we can assume that the unpaired electron is in a d_{z^2} orbital, but is partly delocalized to orbitals on the cyanide ligands; this leads to reduction of the spin–orbit coupling and consequently to a low relaxation rate (see ref. 6) which may permit observation of paramagnetic broadening of the quadrupole lines. Since the precession frequency of the nuclei in the $\pm 3/2$ state is largest, the effect will be more pronounced for the $(\pm 3/2 \rightarrow \pm 1/2)$ line. If the fluctuations are due to electronic spin–spin relaxation, the asymmetry will essentially be independent of temperature, whereas spin–lattice relaxation leads to a decrease in asymmetry with increasing temperature.

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EXPERIMENTAL AND RESULTS

The experimental procedures were essentially the same as described previously.[1,2] Source spectra were recorded at a series of temperatures between liquid-nitrogen and room temperature, and in all cases four different resolutions in Lorentzian lines were attempted: (*a*) in two symmetric doublets; (*b*) in three symmetric doublets; (*c*) in a symmetric doublet and a doublet with lines of equal width, but different intensity; and (*d*) in a symmetric doublet and a doublet with lines of equal intensity but different width.

For low-temperature measurements the resolution (*a*) was unsatisfactory (*e.g.* at 84 K, $\chi^2 = 311$ with a 1% level of 299), but none of the other three possibilities could be excluded on a statistical basis (at 84 K: $\chi^2 = 237$, 295, and 282 respectively). Of these, resolution (*b*) led to roughly the same results as found with the $Cd_3[^{57}Co(CN)_6]_2,12H_2O$ source [2] and it is not discussed further. Resolution (*c*), based on the assumption of a doublet with intensity-asymmetry, corresponds to the assumption of a Goldanskii–Karyagin effect for the $[Fe(CN)_5]^{2-}$ complex. The last resolution, (*d*), corresponds to the assumption of paramagnetic relaxation, although it must be admitted that in such a case the lines are not truly Lorentzian.

The asymmetries, defined as the ratio between the unconstrained parameters, are shown as a function of temperature in the Figure and in both cases disappeared with increasing temperature. For temperatures above *ca.* 200 K, there is no statistical basis for assuming asymmetric doublets. For resolution (*d*) (paramagnetic relaxation), the quadrupole splitting of the symmetric doublet showed the same temperature dependence as that of $[Fe(CN)_6]^{3-}$ in a $Cd_3[Fe(CN)_6]_2,12H_2O$ absorber. The splitting of the asymmetric doublet was 1·6 mm s^{-1}, independent of temperature. The temperature dependence of the intensity of the two doublets was consistent with the assumption of temperature-independent yields of two species with Debye temperatures 260 ± 50 and 160 ± 20 K respectively. Extrapolation of the intensities to 0 K showed that the alleged pentacyanide is formed with a probability of *ca.* 85%.

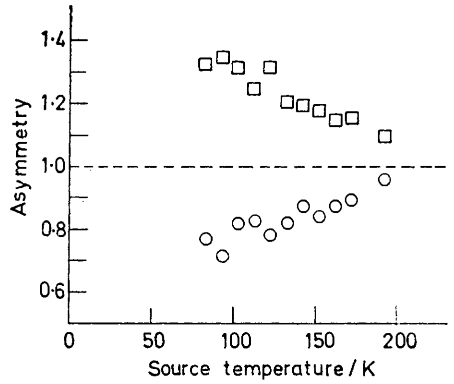
DISCUSSION

The two computer fits of the source spectra with a symmetric and an asymmetric doublet are equally satisfactory from a statistical point of view, but since the asymmetry vanished with increasing temperature a Goldanskii–Karyagin effect in the $[Fe(CN)_5]^{2-}$ complex is excluded. This indicates that ^{57}Fe is more regularly bonded than one would expect by mere loss of a CN^- ligand. The proposed $[Fe(CN)_5]^{2-}$ probably has a structure similar to that of $[Co(CN)_5]^{3-}$, which has been calculated by Guenzburger *et al.*[7] They found that the cobalt must be displaced above the equatorial plane (*i.e.* into the pyramid) and suggest that α (the angle 'axial ligand'–metal–'equatorial ligand') is *ca.* 102°. This value is very close to that reported from *X*-ray structure determinations of square-pyramidal $[Ni(CN)_5]^{3-}$.[8] A displacement of the ^{57}Fe above the equatorial plane would presumably also give a lower electric-field gradient; this is in qualitative agreement with the measured quadrupole splitting of 1·6 mm s^{-1}, which is significantly lower than that normally found for substituted pentacyanoferrate(III) complexes.[9]

In $[Cr(en)_3][Ni(CN)_5],1{\cdot}5H_2O$ (en = ethylenediamine) [8] the root-mean-square amplitudes of vibration for the five-co-ordinate nickel was found to be *ca.* 0·160 Å (at room temperature?). This corresponds to an *f* factor [4] of *ca.* 0·2 and a Debye temperature of *ca.* 165 K, *i.e.* very close to the value we have found for $[Fe(CN)_5]^{2-}$. Since the vibrations of atoms in a lattice do not only depend on the nearest neighbours, this agreement should not be overemphasized, but it shows that our value for $[Fe(CN)_5]^{2-}$ is not unreasonable. The rather crudely determined Debye temperature for $[Fe(CN)_6]^{3-}$ in our sources is not significantly different from that of $[Fe(CN)_6]^{3-}$ in absorbers.[2]

The temperature dependence of the asymmetry of the $[Fe(CN)_5]^{2-}$ doublet seems to exclude fluctuating magnetic fields due to spin–spin relaxation, but is consistent with the assumption of spin–lattice relaxation; this also explains why essentially the same asymmetry was observed in spectra of diamagnetic $Cd_3[^{57}Co(CN)_6]$,-$12H_2O$.[2] Since the low-velocity line is broadest (*cf.* Figure), it must correspond to the $(\pm 3/2 \rightarrow \pm 1/2)$ transition which then has the highest energy. This, in turn, implies that the electric-field gradient is positive, as has been calculated for substituted pentacyanides.[4]

The present report gives an example of the ambiguity which often arises in resolution of complex Mössbauer spectra. The resolution of our spectra into one symmetric and one asymmetric doublet cannot be preferred to a resolution into three symmetric doublets on a purely statistical basis. On the other hand, it offers an interpretation in terms of a simpler, temperature-independent, reaction scheme.



Asymmetry of the outer doublet in the source spectrum of $Cd_3[(^{57}Co)Fe(CN)_6],12H_2O$ defined as: (□), the ratio between the widths of the low- and high-velocity line, assuming equal intensities; and (○), the ratio between the intensities of the low- and high-velocity lines, assuming equal widths

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