Temperature-dependent After-effects of the Cobalt-57–Iron-57 Electron-capture Reaction in $Cd_3[^{57}Co(CN)_6]_2,12H_2O$

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The Mössbauer emission spectrum of $Cd_3[^{57}Co(CN)_6]_2,12H_2O$ was measured at temperatures between 78 and 323 K. Above 200 K the spectra can be resolved into two doublets; one is ascribed to $^{57}Fe(CN)_6^{3-}$ and one to $^{57}Fe(CN)_5^{2-}$; it is suggested that the pentacyanide is formed by a Coulomb explosion following an Auger process associated with the $^{57}Co(EC)^{57}Fe$-decay. Below 200 K a third species is detected; it may be Fe^{2+} formed by cyanide linkage isomerism. Measurements of the total intensity of the spectrum and the relative intensities of the individual doublets as a function of temperature permit in principle a determination of the *f*-factors for the species formed. It is estimated that the $^{57}Fe(CN)_5^{2-}$ has a formal Debye temperature of 170 K; at room temperature it is detected with a probability of only 50% of that of the $^{57}Fe(CN)_6^{3-}$.

MÖSSBAUER spectroscopy is an attractive tool in the study of chemical effects of nuclear reactions, since it offers an analysis which is non-destructive and follows after the nuclear reaction only delayed by a time of the order of the lifetime of the Mössbauer level.[1] The well known $^{57}Co(EC)^{57}Fe$ reaction has naturally received most attention in such studies. The electron-capture decay normally releases an Auger cascade, which may lead to the loss of several electrons;[2] it is therefore not surprising that in Co^{II}-compounds some Fe^{III} is formed, although its way of stabilization is still discussed. In some Co^{III} complexes, however, the chemical effects are more drastic than a mere change in the state of oxidation. In order to explain such observations three mechanisms have been suggested: (1) radiolysis by Auger electrons of the parent complex or of species in its immediate neighbourhood; (2) Coulomb fragmentation of the charged molecule; and (3) molecular excitation, leading to dissociation, caused by the emission and (or) recapture of electrons.

In a recent study of the chemical effects of $^{57}Co(EC)^{57}Fe$ reactions in $^{57}Co(CN)_6^{3-}$ ions,[3] we compared the emission spectra of a series of ^{57}Co-labelled cobaltihexacyanides with bivalent cations. The spectra were resolved into two doublets; one of these has a quadrupole splitting of *ca.* 0·4 mm s^{-1} corresponding to $^{57}Fe(CN)_6^{3-}$.[4] The other doublet has a splitting of *ca.* 1·8 mm s^{-1} and must arise from an ^{57}Fe-labelled species formed as a consequence of the electron-capture reaction. The relative intensity of the resonances from this new species increases with the ionization energy of the cations ($Me^{2+} \longrightarrow Me^{3+} + e^-$). We interpreted these results by assuming that a CN^- ligand is expelled from the complex by Coulomb repulsion to form a pentacyanide, and that the reaction can be prevented if the electrons, lost by the Auger process, can be substituted sufficiently rapidly from the cations.

Such Mössbauer studies have two weaknesses: (1) The *f*-factors of the different ^{57}Fe species formed by the

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[1] A. G. Maddock, in MTP International Review of Science, vol. 8, Butterworths, London, 1972, p. 213.

[2] H. Pollak, *Phys. Stat. Solidi*, 1962, **2**, 720.

[3] J. Fenger, K. E. Siekierska, and J. Olsen, *J.C.S. Dalton*, 1973, 563.

[4] A. Z. Hrynkiewicz, B. D. Sawicka, and J. A. Sawicki, *Phys. Stat. Solidi*, 1970, **38**, K111.

electron-capture reaction may be different (then the species are not detected with the same efficiency) and some may be overlooked completely. (2) The experimental data are often not sufficient for an unambiguous identification of the species; thus in the case of cyanide complexes it is not possible to distinguish between $^{57}Fe^{III}(CN)_5^{2-}$ and $^{57}Fe^{III}(CN)_5(NC)^{3-}$, since the nitrogen end of the CN^- ligand has a low ligand-field strength.[5] Therefore additional evidence is necessary to decide whether a CN ligand is completely lost from the complex or if it only changes its orientation. This again may give information on the mechanism, since an electronic excitation may lead only to a change of the orientation of the CN^- ligand, whereas the Coulomb repulsion probably gives a total bond rupture.

In the present study we have investigated reactions in cadmium cobaltihexacyanide in more detail; this compound was chosen since it was the one which showed the highest yield of pentacyanide in the previous experiments.[3] The results of preliminary experiments on ^{57}Co-doped cadmium ferrihexacyanide are briefly mentioned in order to show that it is of minor importance that ^{57}Fe is born in a ' cobalt-lattice. '

Cobalti- and ferri-hexacyanides with bivalent cations have the general chemical formula $Me_3[Co \text{ or } Fe(CN)_6]_2,nH_2O$; the number of molecules of water of crystallization has not been agreed upon; probably it is of zeolitic nature.[6] A series of these salts including the ones with Cd^{2+} cations form isomorphic crystals of face-centred cubic structure, space group O_h^5–$Fm3m$. The crystals have a main lattice of bivalent cations and complex hexacyanide ions arranged in an NaCl structure and have additional Me^{2+} ions inside some of the small cubic cells.[7-9]

Mössbauer absorption spectra of the ferricyanides exhibit a doublet with a large and strongly temperature-dependent quadrupole splitting. This has been explained[4] as an effect of the Me^{2+} ions outside the main lattice; they give a low-symmetry crystal field, which removes the degeneracy of the t_{2g} level of the Fe^{III} and thereby produces an electric-field gradient. Since the electron population on the sublevels is temperature-dependent, the same will be the case with the electric-field gradient and the resulting quadrupole splitting. The direct effect of the lattice electric-field gradient is small in the temperature region of interest in the present study (*ca.* 80—320 K).[4]

When ^{57}Fe is formed in, *e.g.*, a $Cd_3[^{57}Co(CN)_6],nH_2O$ crystal, and provided that a charge relaxation has prevented chemical effects, the Mössbauer emission spectrum should correspond closely to the absorption spectrum of $Cd_3[Fe(CN)_6]_2,nH_2O$. The quadrupole splitting in the absorber spectrum may however be slightly larger, because some distortion of the $Cd_3[Fe(CN)_6]_2,nH_2O$ is possible.[9] The *f*-factors must in principle be different, but since the crystal structures are nearly identical and the masses of the components are similar, this effect is probably below the accuracy of the measurements.

EXPERIMENTAL

Preparation of Sources and Absorbers.—A source of $Cd_3[^{57}Co(CN)_6]_2,nH_2O$ was prepared as described previously (ref. 3 and refs. therein). The amount of water in the lattice was determined by thermogravimetry to be $n = 12$; dehydration starts slowly just above room temperature and is completed at 120 °C; when the material is stored at room temperature the water is again absorbed from the atmosphere.

A source of $Cd_3[Fe^{57}Co(CN)_6]_2,nH_2O$ was prepared by precipitating the cadmium ferricyanide in the presence of carrier-free $^{57}Co(CN)_6^{3-}$. The number n was found to be 12. Upon heating, $8H_2O$ is lost between room temperature and *ca.* 120 °C; the rest is lost gradually until the material decomposes at 340 °C. Undoped material was used for absorber measurements.

The sources were mounted in aluminium holders, tightly closed with a 1 mm Perspex lid. Absorbers were mounted in aluminium rings between layers of Scotch tape.

Mössbauer Measurements.—Mössbauer spectra were recorded at temperatures between 78 and 323 K with a conventional spectrometer operating in time mode. The sources were measured with a $K_4Fe(CN)_6,3H_2O$ absorber (1 mg $^{57}Fe/cm^2$; 91% enriched) kept at room temperature. The absorbers were measured with a $Pd(^{57}Co)$ source, likewise kept at room temperature.

Sums of Lorentzian lines were fitted to the experimental spectra by means of a computer programme[10] based on the Gauss non-linear regression procedure. One, two, or three doublets of lines with equal width and intensity were assumed, but all other parameters were left free to vary during the fitting procedure. The size of the error bars shown on the Figures are average values of the standard deviations calculated by the programme; these values are in good agreement with the results of duplicate measurements.

Treatment of the Data.—The resonances observed in the absorber spectra were transformed to a hypothetical source experiment by a correction for the isomer shift between the $Pd(^{57}Co)$ source and the $K_4Fe(CN)_6,3H_2O$ absorber followed by a change of sign of the resulting isomer shifts. The resonance positions thus found were used for identification of the resonances in the source spectra (*cf.* Figure 1).

The resonance intensities were calculated from the areas under the fitted Lorentzian lines and expressed in units of percent. absorption/(mm $s^{-1})^{-1}$. For the source spectra also the total intensity of the spectra was calculated; this intensity is more accurately determined than the intensity of the resonances of individual species, since the fitted parameters are correlated.

In the high-temperature limit, *i.e.*, for most inorganic solids above liquid-nitrogen temperature the *f*-factor can be approximated by[11] equation (1) where E_r is the γ-recoil

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[5] D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, 1965, **4**, 725.

[6] H. B. Weiser, W. O. Milligan, and J. B. Bates, *J. Phys. Chem.*, 1941, **45**, 701.

[7] A. Ferrari, M. E. Tani, and G. Magnano, *Gazzetta*, 1959, **89**, 2512.

[8] A. K. van Bever, *Rec. Trav. chim.*, 1938, **57**, 1259.

[9] H. B. Weiser, W. O. Milligan, and J. B. Bates, *J. Phys. Chem.*, 1942, **46**, 99.

[10] A. J. Stone, H. J. Aagaard, and J. Fenger, Risö-M-1348, Feb. 1971.

[11] N. N. Greenwood and T. C. Gibb, ' Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.

energy (1·95 × 10^{-3} eV in case of ^{57}Fe), k is the Boltzmann constant (0·862 eV K^{-1}), T is the absolute temperature, and

$$f = \exp \frac{-6E_rT}{k\theta_D^2} \qquad (1)$$

θ_D is a Debye temperature. For a sufficiently thin absorber it is therefore possible to determine θ_D by plotting the logarithm of the resonance intensity against T. By extrapolating the curve to $T = 0$, where the model requires that $f = 1$, we can further correct the resonance intensity for the f-factor of the source and thus obtain an expression for the f-factor of the absorber.[14]

We have also used this procedure for sources. In principle a correction should be made for the temperature-dependent self-absorption in the source material; however the source can easily be made thin, and the γ-quanta are often emitted from species other than those of the matrix. When the source matrix is a cobalt compound, it further only contains ^{57}Fe formed by decay of ^{57}Co or present as impurities. Our measured resonances are therefore plotted directly. It should be stressed that θ_D values, especially when determined for sources, are not very closely related to the lattice properties, but they are convenient parameters for a description of the experimental results.

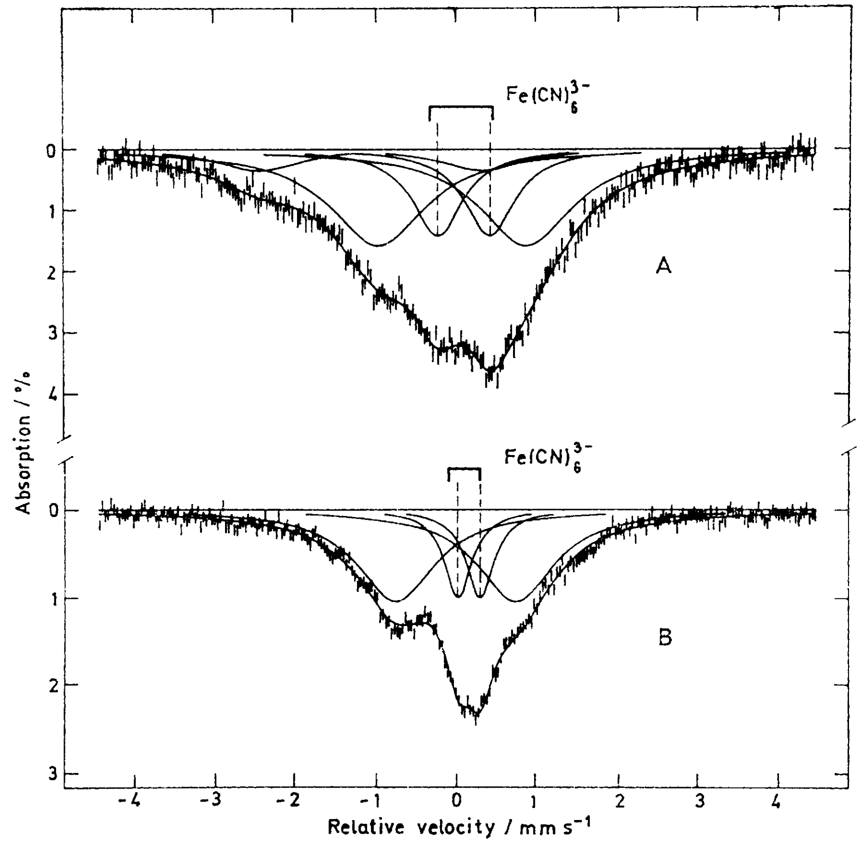

FIGURE 1 Mössbauer emission spectra of $Cd_3(^{57}Co(CN)_6]_2,12H_2O$ as source recorded at A, 113 and B, 295 K with a $K_4{}^{57}Fe(CN)_6,3H_2O$ absorber. The resonance positions for $Fe(CN)_6{}^{3-}$ are determined from spectra of a $Cd_3[Fe(CN)_6]_2,12H_2O$ absorber. The section between the vertical broken lines refers to $Fe(CN)_6{}^{3-}$

The discussion of the results is based on a comparison between spectra recorded with sources and absorbers as a function of temperature. The parameters of the absorber spectra are much better determined than those of the complex source spectra; therefore the ' absorber-results ' are only presented as curves, whereas the ' source-results ' are plotted individually.

RESULTS AND DISCUSSION

Emission spectra of $Cd_3[^{57}Co(CN)_6]_2,12H_2O$ recorded above 150 K could be satisfactorily accounted for with two doublets as previously observed.[3] At lower temperatures, however, it was necessary to assume an extra resonance at −3 mm s^{-1}. Since no species with so large isomer shifts are known, we assumed that this resonance is part of a doublet and we consequently fitted the spectra with three doublets. With the parameters found for the low-temperature spectra as initial estimates, it was possible to fit three doublets also to spectra recorded at *ca.* 200 K; the intensity of the extra doublet was, however, of the order of the uncertainty. Two typical spectra are shown in Figure 1.

The isomer shift and quadrupole splitting of the narrowest doublet in the source spectra are similar to those of transformed absorber spectra of $Cd_3[Fe(CN)_6]_2$,-$12H_2O$; the quadrupole splittings are compared in Figure 2. We therefore ascribe this doublet to $^{57}Fe(CN)_6{}^{3-}$ in normal lattice positions. The strongest doublet has a quadrupole splitting of *ca.* 1·8 mm s^{-1} and is ascribed to a pentacyanide. The line-width of the pentacyanide resonances is significantly larger than those of Fe(CN)$_6^{3-}$ and also larger than one would expect from absorber measurements;[3] therefore the pentacyanide may be situated in various, slightly different surroundings.

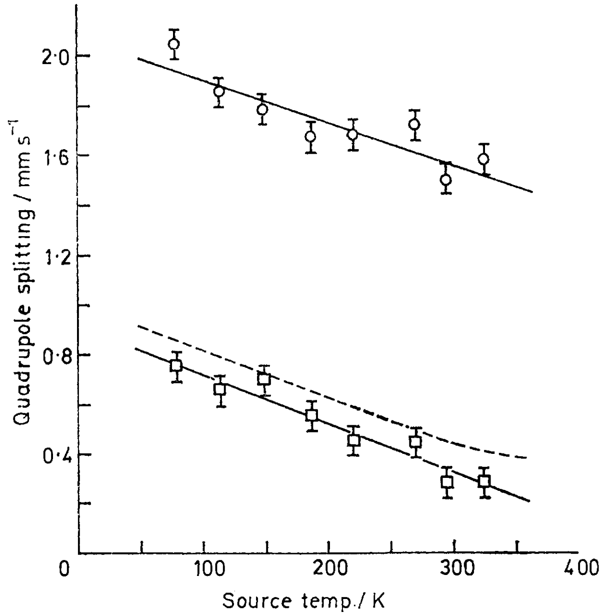

FIGURE 2 Quadrupole splittings for the two strongest doublets in the emission spectrum of $Cd_3[^{57}Co(CN)_6]_2,12H_2O$ as a function of temperature; □, $Fe(CN)_6^{3-}$; ○, $Fe(CN)_5^{2-}$. The quadrupole splitting in the absorber spectrum of $Cd_3[Fe(CN)_6]_2,12H_2O$ is shown with a broken line

The temperature-dependence of the quadrupole splittings of the two cyanide complexes is, within the accuracy of the measurements, the same (*cf.* Figure 2). This can hardly be due to a common lattice contribution, since the direct effect on the Fe(CN)$_6^{3-}$ is small;[4] further it appears that at least in substituted cyanides the electric-field gradient is generated almost entirely by asymmetric covalent bonding of the 3*d* orbitals.[11] We therefore assume that also in the pentacyanide the temperature-dependence is related to a t_{2g} splitting.

The identity of the third, weak doublet, is not clear. The quadrupole splitting can only be determined to be *ca.* 3 mm s^{-1} since the position of one of the lines is uncertain. Similarly the isomer shift can only be estimated to be *ca.* -1 mm s^{-1}. These values suggest that the doublet arises from Fe^{2+}. Absorber measurements of $Fe_3[Co(CN)_6]_2,12H_2O$[12] yield two doublets, one with a splitting of 2·81 mm s^{-1} (at 77 K) arises from Fe^{2+} in the main lattice and one with a splitting of 1·82 mm s^{-1} arises from Fe^{2+} inside the cubic cells. Therefore, if the weak doublet in the source spectra arises from Fe^{2+}, this sits rather in the main lattice than inside the cells. In other words, the Fe^{2+} must have been formed by flip of all six ligands. Alternatively one might imagine the formation of a tetracyanide; it would probably have a larger quadrupole splitting than a pentacyanide, but hardly the observed -1 mm s^{-1} isomer shift.

In principle the asymmetry in the low-temperature spectra could have been accounted for by a magnetic hyperfine interaction. However, we do not consider ferromagnetism likely, since the Curie temperature of similar compounds (Mn, Cu, and Ni ferricyanides) is of the order of 20 K.[13] Paramagnetism is not probable

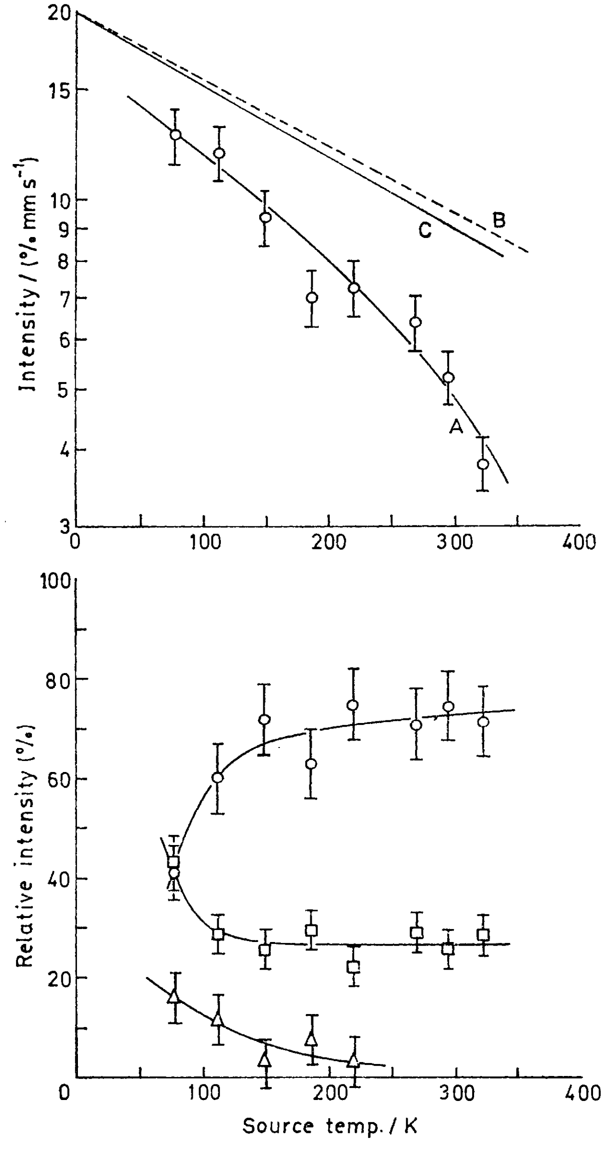

FIGURE 3 Resonance intensities of the emission spectra of $Cd_3[^{57}Co(CN)_6]_2,12H_2O$ (curve A). In the upper, semi-logarithmic, plot the temperature-dependence of the total intensity is compared with that of a $Cd_3[Fe(CN)_6]_2,12H_2O$ absorber, shown with a dashed line (B) and in arbitrary units. The line C corresponds to $\theta_D = 227$ K, an average value for inorganic solids.[14] The lower plot shows the relative intensities of the three doublets in the spectra: ○, $^{57}Fe(CN)_5^{2-}$; □, $^{57}Fe(CN)_6^{3-}$; △, presumably $^{57}Fe^{2+}$.

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[12] K. Maer, M. L. Beasley, R. L. Collins, and W. O. Milligan, *J. Amer. Chem. Soc.*, 1968, **90**, 3201.

[13] B. Sawicki, J. Sawicki, and A. Z. Hrynkiewicz, *Sov. Phys. Sol. Stat.*, 1967, **9**, 1100.

either, since nearly the same spectra were obtained with ^{57}Co-doped $Cd_3[Fe(CN)_6]_2,12H_2O$.

In the upper part of Figure **3** the temperature-dependence of the total intensity of the emission spectrum of the $Cd_3[^{57}Co(CN)_6]_2,12H_2O$ source is compared with that of a $Cd_3[Fe(CN)_6]_2,12H_2O$ absorber. The intensity of the absorber spectrum depends exponentially upon the absolute temperature corresponding to a Debye temperature of 234 ± 4 K. This result is not much different from Kerler's [14] value (227 K) found for a series of inorganic salts, including $K_3Fe(CN)_6$. The intensity of the emission spectrum depends more strongly upon the temperature; although the accuracy of the measurements is modest, it even seems that the slope of the curve increases with temperature. Our preliminary experiments with a ^{57}Co-doped $Cd_3[Fe(CN)_6]_2,12H_2O$ source showed a similar strong temperature-dependence of the resonance intensity; therefore the effect cannot be due to the ^{57}Fe being formed in a 'Co-lattice.' If we reasonably assume that $^{57}Fe(CN)_6{}^{3-}$ in the source has the same f-factor as in the absorber, we must conclude that in the source another ^{57}Fe-labelled species is formed and that it has a lower formal θ_D than $Fe(CN)_6{}^{3-}$. Since a sum of exponential functions with negative exponents would give a curve, which has a decreasing slope, we are forced to conclude that the relative yield of the less tightly bonded species increases with temperature.

The lower part of Figure **3** shows how the relative intensities of the three doublets vary with the temperature of the source, and we note that the relative intensity of the alleged pentacyanide increases. This can account for the temperature-dependence of the total intensity of the source spectrum, especially if the pentacyanide is of the form $Fe^{III}(CN)_5{}^{2-}$, which is only bonded with five bonds in the lattice. The alternative possibility of a $Fe^{III}(CN)_5(NC)^{3-}$ species is less likely; not only is the isocyanide bonded with six bonds, but it also appears [15,16] that the isocyanides are stable only at low temperature. Their yields should therefore presumably decrease with temperature.

On the other hand, if we assume that a CN^- ligand is lost completely by Coulomb repulsion, and that the process can be prevented by charge transfer from the surroundings, one might again expect a decrease of the pentacyanide with temperature. The Prussian blue-type crystals are intrinsic semiconductors [17] and charge transfer is therefore facilitated at higher temperatures. It is, however, reasonable to assume that an expelled CN^- ligand is not displaced far from the remaining pentacyanide, since the total Coulomb energy of the charged complex may only be of the order of 25 eV. At low temperatures the fragments may recombine before emission of the Mössbauer quantum to give the parent hexacyanide, whereas at higher temperatures diffusion of the CN^- may be facilitated and recombination prevented. In case the fragments do not recombine, nearby CN^- in various positions may account for the broad resonance lines of $Fe(CN)_5{}^{2-}$.

The nature of the third species, which is observed only at temperatures below about 200 K, is still not clear. The temperature-dependence of the resonance intensity can be accounted for with a formal Debye temperature of about 100 K, but we cannot suggest any species sufficiently weakly bonded in the lattice to give this figure. Therefore the yield probably increases with decreasing temperature; the possibility of Fe^{2+} in a lattice position, formed by inversion of six CN ligands, is thus still open. Cyanide linkage isomerism has been observed before [18] although the mechanism seems to be more complicated than a simple cyanide flip.

From the total intensity extrapolated to $T = 0$ and the relative intensities at a temperature, *e.g.*, room temperature, where only hexacyanide and pentacyanide are observed it is, in principle, possible to determine the formal Debye temperature of the pentacyanide. With the present inaccurate data, we can only estimate it to be of the order of 170 K. At room temperature, this means that the pentacyanide is detected with an efficiency which is only 50% of that of the hexacyanide. If we, to a very rough approximation, consider ^{57}Fe in $Fe(CN)_5{}^{2-}$ as sitting in the surface of a hole, it is found that these values are not unreasonable (*cf. e.g.*, ref. 19).

The present studies have demonstrated that different species formed by nuclear decay in solids can have significantly different formal Debye temperatures; this must be taken into account when Mössbauer spectroscopy is used in studies of chemical effects of nuclear transformations. The low Debye temperature for the observed pentacyanide suggests that it is $Fe(CN)_5{}^{2-}$; this supports our hypothesis [3] that the nascent ^{57}Fe-labelled hexacyanide can be ruptured by Coulomb repulsion.

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