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MÖSSBAUER SPECTROSCOPIC STUDIES ON CRYSTALLOGRAPHIC PHASE TRANSITION IN $Fe(py)_2Cl_2$ AND α-$Co(py)_2Cl_2$

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Anomalies were found in the temperature dependence of quadrupole splitting of ^{57}Fe in $Fe(py)_2Cl_2$ and α-(^{57}Co, Co)$(py)_2Cl_2$ at 228°K and 160°K, respectively, when these compounds were prepared by "wet method". The X-ray powder patterns of the compounds also show slight changes at the same temperatures. It was found that the materials prepared by "dry method" remain in the high temperature phase even below the phase transition temperature.

We previously reported that the "polymer effect" was observed in the recoil-free fraction of ^{57}Fe produced in α-$Co(py)_2Cl_2$ containing ^{57}Co as a Mössbauer source nuclide and that the quadrupole splitting at 80°K is anomalously large compared to that at room temperature.[3] In the course of the experiment, we have found that the quadrupole splitting of ^{57}Fe in $Fe(py)_2Cl_2$ and of ^{57}Fe produced in ^{57}Co-labelled α-$Co(py)_2Cl_2$ changes markedly at 228°K and 160°K, respectively.[4] Recently, an anomaly in the magnetic susceptibility anisotropy of this compound at the same temperature has been reported by Bentley *et al.*[5] The facts may imply that the quadrupole splitting of ^{57}Fe produced in α-$Co(py)_2Cl_2$ depends on the crystallographic property of the host cobalt compound rather than that of the neat iron compound. Long *et al.* have found that $Fe(py)_2Cl_2$ undergoes a transformation at lower temperatures on the basis of the Mössbauer spectral properties of the two preparations, although they have reported no detailed information on the transition temperature.[6] We have undertaken the present work to elucidate the temperature dependence of quadrupole splitting of ^{57}Fe both in $Fe(py)_2Cl_2$ and α-$Co(py)_2Cl_2$.

$Fe(py)_2Cl_2$ was prepared by heating $Fe(py)_4Cl_2$ in hot methanol as described in

Ref. 7 (thereafter we call it wet method). It has been reported that this compound is obtained by thermal decomposition of $Fe(py)_4Cl_2$ under nitrogen.[8] The latter

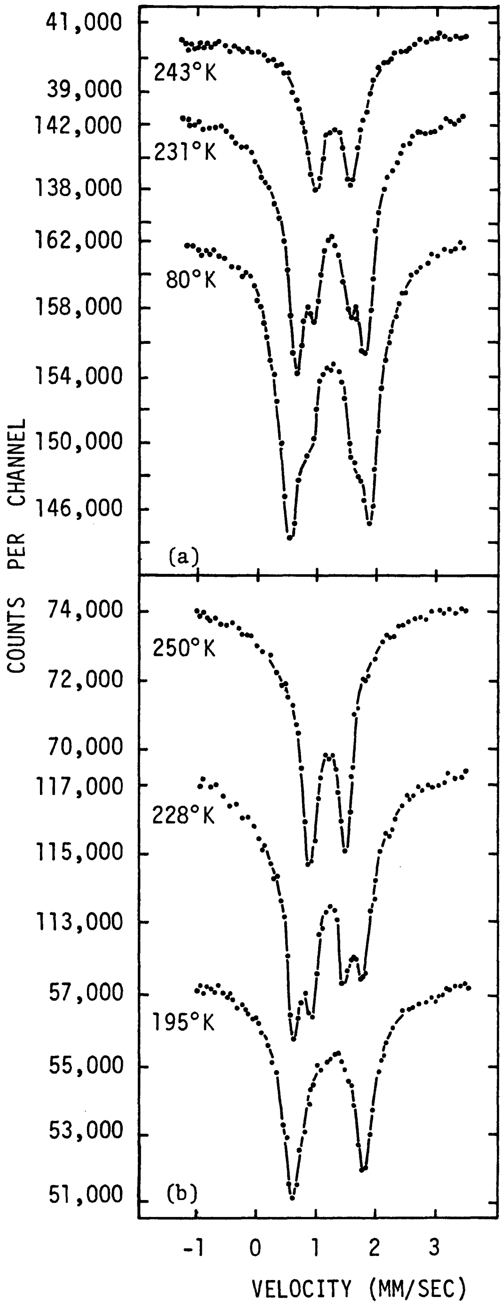

Fig. 1. The Mössbauer spectra of $Fe(py)_2Cl_2$ absorbers prepared by "dry method" (a), and "wet method"(b), at various temperatures using a $^{57}Co(Cu)$ source. The velocity scale was normalized with respect to iron.

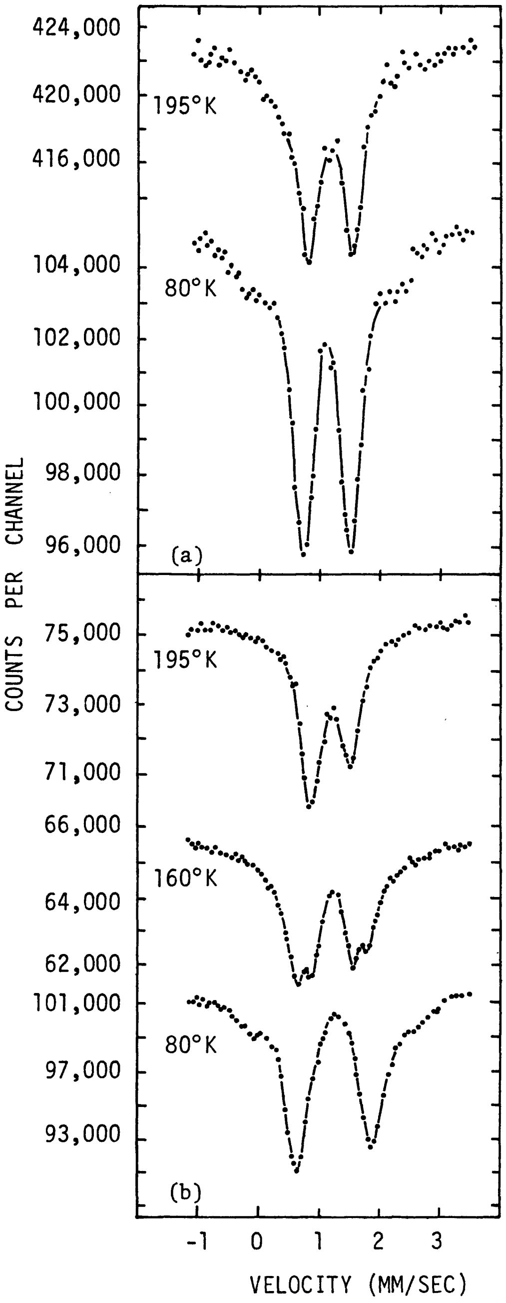

Fig. 2. The Mössbauer spectra of α-($^{57}Co,Co)(py)_2Cl_2$ sources prepared by "dry method" (a), and "wet method" (b), at various temperatures using a stainless steel absorber. The velocity scale was normalized with respect to iron.

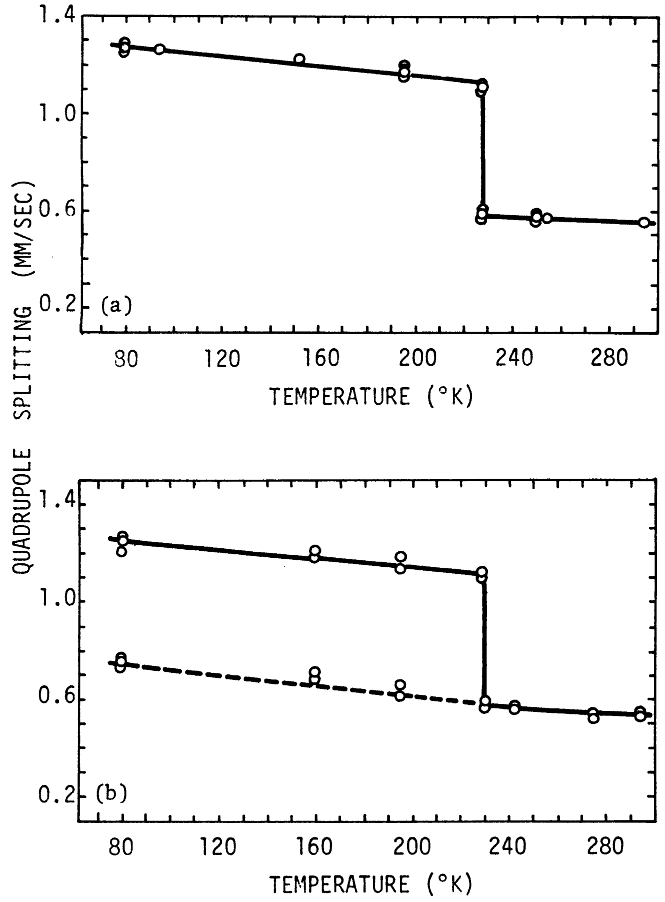

Fig. 3. The temperature dependence of the quadrupole splitting of $Fe(py)_2Cl_2$ prepared by "wet method" (a), and "dry method" (b). Broken line indicates the temperature dependence of the quadrupole splitting of the inner doublet.

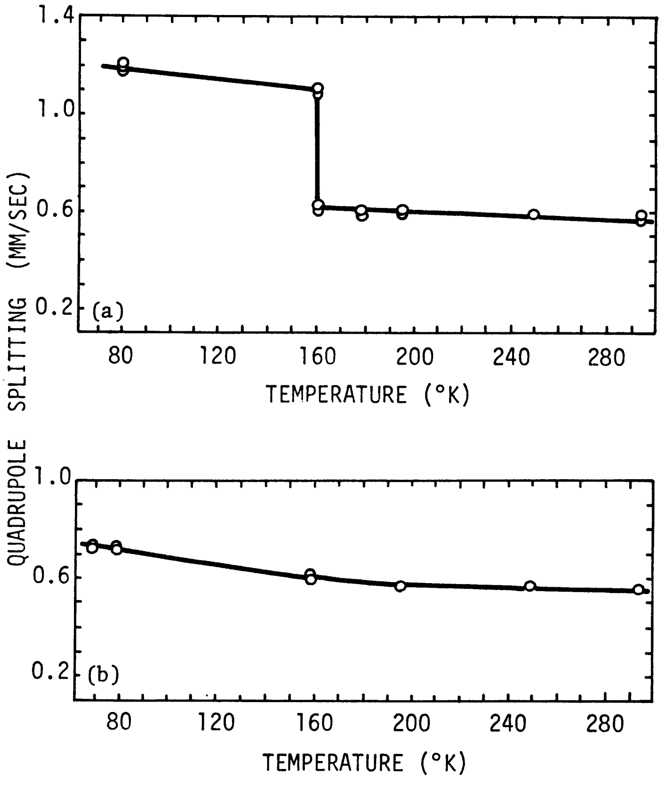

Fig. 4. The temperature dependence of the quadrupole splitting of α-$^{57}Co(py)_2Cl_2$ prepared by "wet method" (a), and "dry method" (b).

method (dry method) was also used to prepare the compound. ^{57}Co-labelled α-$Co(py)_2Cl_2$ was prepared from cobalt(II) chloride solution containing 1 mCi ^{57}Co by following the method described in Ref. 9 (wet method). Similarly to $Fe(py)_2Cl_2$, the dry method was also used to prepare the compound, since it is known that the compound is obtained by thermal decomposition of $Co(py)_4Cl_2$.[10] The Mössbauer spectra were measured by using a constant acceleration drive described elsewhere.[3,4] The X-ray powder patterns of these compounds were taken using Co-Kα radiation at various temperatures controlled with a liquid-nitrogen heater system.

Figs. 1 and 2 illustrate typical Mössbauer spectra of these compounds at various temperatures. The spectra of $Fe(py)_2Cl_2$ made by the wet method show a doublet with an isomer shift value typical of a high-spin ferrous compound. Upon cooling, two other lines appear outside of the original doublet at 228±1°K. Similar temperature dependence is observed in $Fe(py)_2Cl_2$ prepared by the dry method, but the inner doublet remains even below 228°K, as shown in **Fig. 1a**. The temperature dependence of the quadrupole splitting of ^{57}Fe produced in α-$Co(py)_2Cl_2$ prepared by the wet

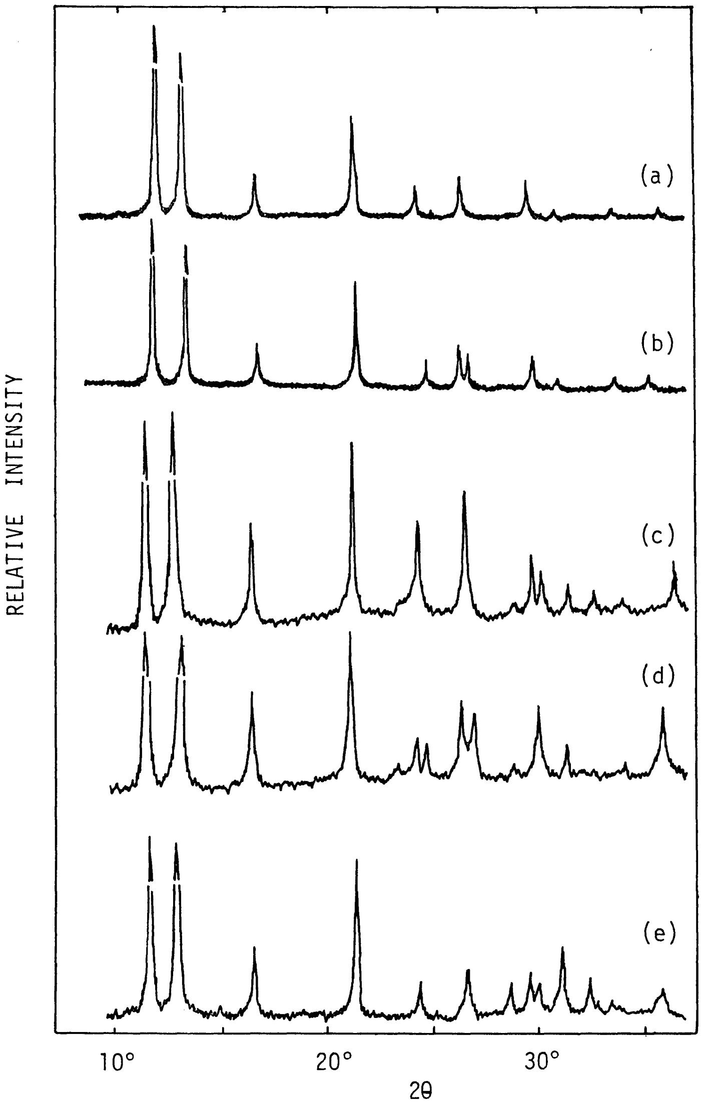

Fig. 5. The X-ray powder patterns of $Fe(py)_2Cl_2$ and α-$Co(py)_2Cl_2$. (a) $Fe(py)_2Cl_2$ (wet method) above 228°K, (b) $Fe(py)_2Cl_2$ (wet method) below 228°K, (c) α-$Co(py)_2Cl_2$ (wet method) above 160 °K, (d) α-$Co(py)_2Cl_2$ (wet method) below 160°K, and (e) α-$Co(py)_2Cl_2$ (dry method) at any temperature from 70 to 300°K.

method shows the discontinuity at 160 ± 1°K, whereas α-(^{57}Co, Co)(py)$_2$Cl$_2$ made by the dry method shows no such discontinuity at the temperature range from 78 to 300°K, as seen in Figs. 3 and 4.

Temperature dependence of the X-ray powder diffraction pattern of these compounds indicates a slight change at 228°K for Fe(py)$_2$Cl$_2$ and 160°K for α-Co(py)$_2$Cl$_2$ prepared by the wet method but no change for α-Co(py)$_2$Cl$_2$ made by the dry method, as illustrated in Fig. 5.

The values of recoil-free fraction for the ^{57}Co-labelled α-Co(py)$_2$Cl$_2$ source and Fe(py)$_2$Cl$_2$ absorber were estimated from the area of the spectrum by following Lang's method,$^{11)}$ by comparing these with the result of the stainless steel versus ^{57}Co(Cu) source. The values of recoil-free fraction of the copper and the stainless steel were assumed to be 0.72 and 0.82 at room temperature, respectively.$^{12)}$ Although there would be some ambiguity in the absolute value of the recoil-free fraction of ^{57}Fe in copper and stainless steel, the temperature dependence of the recoil-free fraction of these samples could be reliable when the slopes were compared. Fig. 6 illustrates the temperature dependence of recoil-free fraction of these samples. A greater temperature dependence observed in α-(^{57}Co, Co)(py)$_2$Cl$_2$ source may be attributed to the radiation effect due to EC-decay and Auger processes.

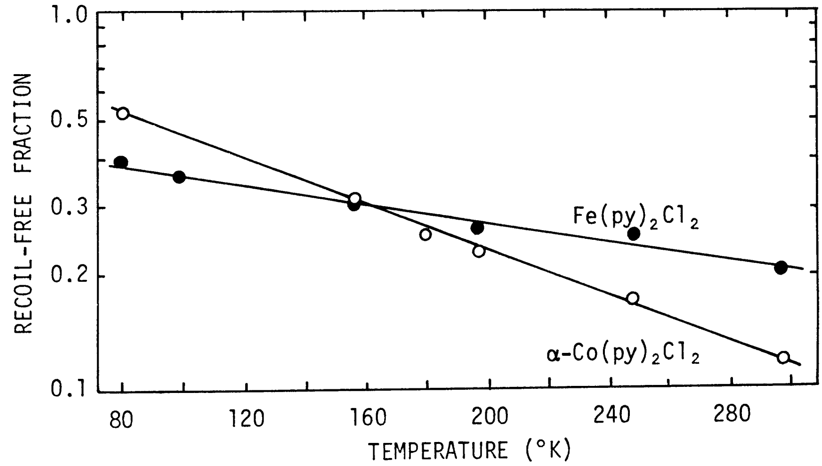

Fig. 6. The temperature dependence of the recoil-free fraction (log base 10 scale) for Fe(py)$_2$Cl$_2$ and α-(^{57}Co, Co)(py)$_2$Cl$_2$.

There seems no appreciable discontinuity in the temperature dependence of the isomer shifts or the recoil-free fractions in either $Fe(py)_2Cl_2$ or α-$Co(py)_2Cl_2$ in the pertinent temperature range. This implies that the phase transition involves neither change of *s*-electron density at ^{57}Fe nucleus nor significant change of crystal structure. This may be consistent with the very slight change found in the temperature dependence of the X-ray powder diffraction pattern of these compounds. The differential thermal analysis of these compounds shows no appreciable peak at 160°K and 228°K, indicating a possibility of the second order phase transition.

These results suggest that some conformational changes around metal atoms, such as changes of the angle of Cl-Fe-Cl or py-Fe-py, librational condition of pyridine rings around its bonding axis, may occur at 228°K in $Fe(py)_2Cl_2$ and 160°K in α-$Co(py)_2Cl_2$. The materials prepared by the dry method seems to remain in the high temperature phase even at low temperature as a metastable state, in which the polymers are stuck more randomly compared to the materials made by the wet method and the phase transition may be hindered.

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