MÖSSBAUER SPECTROSCOPIC STUDIES OF THERMAL DECOMPOSITION

OF ALKALI FERRICYANIDES

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ABSTRACT

The thermal decomposition of hydrated (Li and Na) and anhydrous (K and Rb) alkaliferricyanides upto 650°C are reported using the Mössbauer Spectroscopic technique. The presence of water brings down the decomposition temperature and also causes the formation of Fe_2O_3 at higher temperature. In the case of anhydrous complexes the end product is iron metal, while in the case of hydrated complexes, superparamagnetic Fe_2O_3 results.

A reaction scheme is proposed which is compatible with the reported DTA and DGE results.

INTRODUCTION

The ferro- and ferricyanides and their derivatives have been the
most favourite low spin iron compounds for the Mössbauer spectroscopic studies,
and by now, a great wealth of data dealing different aspects is made availa-
ble[1-4]. These compounds are very stable and the anion structure remains un-
disturbed in most of the chemical reactions. Seifer and co-workers[5-6] have
investigated systematically a number of cyanoferrates(II) using thermographic,
X-ray, chemical analysis and Mössbauer spectroscopy. They concluded that the
temperature at which the cyanoferrate (II) ion decomposed was inversely depen-
dent on the ionic potential, i.e., charge to radius ratio or polarizing power
of the associated cation. The process of decomposition of hydrated compounds,
viz., hydrolytic or nonhydrolytic also depends on the ionic potential of the
cation. Furthermore, they also noted that at least in the first transition
series, the temperature of initial decomposition was lower when the associated
cation has an odd number of d electrons in its central shell. In their latest
paper[6] they have also shown the usefulness of the Mössbauer spectroscopy
not only in confirming the results obtained by other techniques, but also ena_
bling to follow individual details in these processes with relaible accuracy.
Over and above, the Mössbauer spectroscopy is nondestructive and gives
insitu results. It is surprising that relatively very few such studies are
reported for ferricyanides[4,7,8].

While investigating the 2MeV electron-irradiated alkali fer-
ricyanides using Mössbauer spectroscopy[9], we observed that the presence of
water entangled or as a part of lattice (water of crystallization) plays an
important role in the reduction of iron charge state. It was noticed that,

while reduction was observed in the case of hydrated complexes with small dose, there was no detectable reduction in the anologous anhydrous complexes. Some effect of the presence of water in the thermal treatment is also reported in the literature[4,8,10]. For example, it was observed that in the presence of water vapours the thermal decomposition of $H_4[Fe(CN)_6]$ takes place at much lower temperature. Further, it has been shown[10] that the low temperature. solid state reactions of iron(II) hexacyanochromate, a Prussian Blue type material, were catalyzed by water vapour. Chamberlain and Greene[8] have studied the thermal decomposition of hexacyanoferrates(II) and (III) and of certain nitrosylferrates using differential thermal analysis (DTA) and dynamic gas evolution (DGE) techniques. They suggest that after ejection of water of crystallization the C_2N_2 gas is released resulting in the reduction of iron ion, and that the compounds formed, as thermal decomposition proceeds, contain the iron metal in successively lower formal oxidation states. Furthermore, they observed that the iron(III) complexes decompose at markedly lower temperature than the analogous iron(II) complexes. Also the C_2N_2 evolution in the case of anhydrous salts was comparably at higher temperatures. To further invoke the role of water in the thermal decomposition process and in the absence of any systematic Mössbauer studies of thermal decomposition of ferricyanides, we thought it worthwhile to undertake this work.

EXPERIMENTAL

The complexes selected were the same as for the irradiation[9] experiment, viz., hydrated ferricyanides of Li and Na and anhydrous ferricyanides of K and Rb. Two procedures for heating were adopted. In the first case the samples were heated at different temperatures in pyrex glass capsules under vacuum ($\sim 10^{-2}$ tor.) and their room temperature Mössbauer spectra were recorded

using 5 mCi ^{57}Co:Pd source and Mössbauer spectrometer in constant acceleration mode. Thus for each temperature fresh sample was used. This type of heating was done only for low temperatures. In the second case, the ELRON Mössbauer Vacuum Furnace was used and the complexes were heated successively at higher temperatures for 4 hours at each temperature. In the case of Na and K complexes, each representing a typical of hydrated and anhydrous form, the temperature was increased by 50° increments upto 650°C. After each heating, the furnace was left to cool down to room temperature and the Mössbauer spectra were recorded having the absorber in the furnace itself and with maintained vacuum. Thus, contrary to the first procedure, in this case, the same sample was heated at all the temperatures for four hours at each temperature (Except in the Li case where a direct heating at 520° was done). The vacuum pump was kept on and thus any gas evolved in the process was pumped out. The spectra so obtained are presented in Fig. 1 to 6. A further analysis using solvent extraction technique was made to identify the decomposition products. The magnetization measurements were made using the vibrating sample magnetometer model 155,Princeton Applied Research, U.S.A.

RESULTS AND DISCUSSION

It is evident from the figures that in the presence of water, thermal decomposition takes place at comparably lower temperatures.For example, while in the case of Li and Na complexes the reduction was observed between 100 to 160°C, in the case of K and Rb no noticeable reduction occurred even upto 200°C. This effect of water was further confirmed by partially dehydrating the Na salt and by adding water to K-salt and looking for the termal decomposition temperatures.Whereas,in the Na case the reduction emperature went up,in the K case the reduction was observed at about 170°C(fig.).Furthermore,

to the limit of detectability of other formed specieces, we have noticed that at comparably low temperature the primary process is the reduction, although the formation of other polymers of Prussian Blue type complexes in small amounts cannot be ruled out entirely. These are quite apparent at higher temperatures.
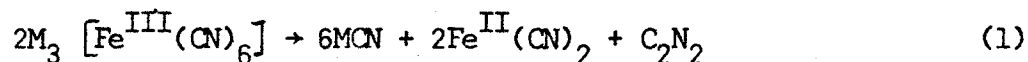
In the case of Na-compound even upto $220^{\circ}C$ the main product was ferrocyanide as can be seen from the Fig.8. Here we have made use of the Dimetheleamide solvent in which the ferrocyanide is insoluble while the ferricyanide is completely soluble.
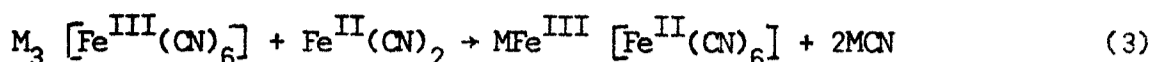
At higher temperatures (at about $300 - 350^{\circ}C$), the iron ions come out of the anion structure and formation of Prussian Blue and ferrous cyanide type structure is evident from the Mössbauer spectra. At about $400-450^{\circ}C$ the formation of cementite (Fe_3C) compound is visible and this on further heating goes to Fe and Fe_2O_3 in anhydrous and hydratad complexes respectively. The spectra at high temperatures are usually very complex due to the presence of admixture of variety of end products.

The probable mechanism of decomposition and the role of water in lowering the decomposition temperature can be understood with the following reaction scheme:
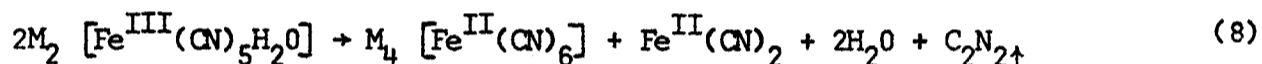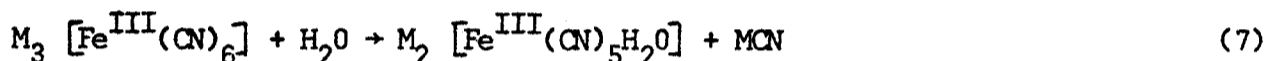
ANHYDROUS COMPLEXES

The decomposition starts with the Eq.(1) and is followed by Eqs. 2-6 as the temperature is increased.

$$2M_3\left[Fe^{III}(CN)_6\right] \rightarrow 6MCN + 2Fe^{II}(CN)_2 + C_2N_2 \tag{1}$$

$$4MCN + Fe^{II}(CN)_2 \rightarrow M_4 \left[Fe^{II}(CN)_6\right] \tag{2}$$

$$M_3 \left[Fe^{III}(CN)_6\right] + Fe^{II}(CN)_2 \rightarrow MFe^{III} \left[Fe^{II}(CN)_6\right] + 2MCN \tag{3}$$

$$3Fe^{II}(CN)_2 \rightarrow Fe_2^{II}\left[Fe^{II}(CN)_6\right] \tag{4}$$

$$3Fe^{II}(CN)_2 \rightarrow Fe_3C + 3N_2 + 5C \text{ (at about } 400^{\circ}C) \tag{5}$$

$$Fe_3C \rightarrow 3Fe + C \tag{6}$$
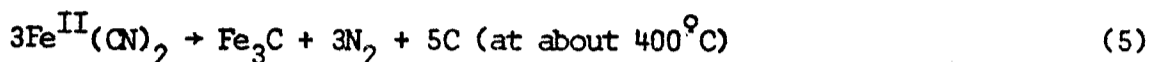
HYDRATED COMPLEXES

In the case of hydrated complexes the water first replaces one of the cyanogen group to form an aquopentacyano complex (Eq. 7) which further decomposes according to Eq. 8 and then the reactions of Eq. 2 to 6 may follow.

$$M_3 \left[Fe^{III}(CN)_6\right] + H_2O \rightarrow M_2 \left[Fe^{III}(CN)_5H_2O\right] + MCN \tag{7}$$

$$2M_2 \left[Fe^{III}(CN)_5H_2O\right] \rightarrow M_4 \left[Fe^{II}(CN)_6\right] + Fe^{II}(CN)_2 + 2H_2O + C_2N_2\uparrow \tag{8}$$

The reaction of Eq. 8 occurs around $100^{\circ}C$ to $200^{\circ}C$ depending on the heating process. The replacement of a CN group by water (Eq. 7) requires less energy as compared to the complete breaking up of the complex (Eq.1) and thus explains the lowering of the decomposition temperature. In the limit of detectability no Mössbauer spectrum for the aquopentacyano complex was, noted. The assumption that this intermediate complex actually decomposes at these temperatures was separately checked and found satisfactory (Fig.9).Formation of aquopentacyanoferrate(II) in the solution of $K_4Fe(CN)_6$, when the latter is exposed to ultraviolet light is well known.[11] A similar explanation was gi-

ven by Fanning et al.[4] to account the lowering of the temperature of forma tion of Prussian Blue from $H_4Fe(CN)_6$ in the presence of water vapour. It is surprising that no such effect of water in the case of $H_3Fe(CN)_6$ heating was detected. The formation of Prussian Blue type complexes at higher temperatures are also reported by other authors[5,7] when complex ferricyanides and ferrocyanides were heated. In the case of hydrated complexes further reactions of the following type also occur, which explain the formation of the ferric oxide.

$$MCN + H_2O \rightarrow MOH + HCN \qquad (9)$$

$$6MOH + 4Fe \rightarrow 2Fe_2O_3 + 3H_2 + 6M \qquad (10)$$
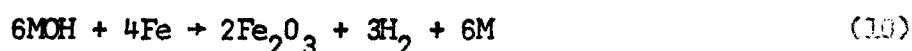
The last reaction is reported to start at about $500^\circ C$ in vacuum and at $650^\circ C$ approximately 70 to 80 percent of the metal is turned into oxide.[12] It is interesting to note that no such ferric oxide formation was observed[7] in the thermal decomposition of $Eu [Fe(CN)_6]$.$5H_2O$ in vacuum. This may be explained on the fact that the alkali hydroxides are much more reactive than the europium hydroxide, which might have also been formed in the heating process. Some of these reactions are on the lines of Seifer[5,6] et al., who systematically explained the decomposition of the ferrocyanide complexes.

In the case of Na ferricyanide the magnetic-split well defined spectrum, besides a central part, at $500^\circ C$ is that of Fe_3C and its peak positions and the magnitude of the internal magnetic field (~210 KOe) are in good agreement to those reported in the literature.[13÷15] The complex nature of the spectrum at $550^\circ C$ can be attributed to the simultaneous presence of Fe_3C, Fe, and Fe_2O_3 the latter with variety of particle sizes. The central part of this spectrum is a doublet, which arises due to the superparamagnetic behaviour of very fine Fe_2O_3 particles.[16]. This is further confirmed by the

spectra with 600 and 650°C heating. Li ferricyanide is a similar hydrated complex case. Directly heating to 520°C leads to the superparamagnetic state of formed Fe_2O_3, which is more clearly evident in the spectrum with 620°C heating. This end product was subjected to the magnetic susceptibility measurements to confirm the superparamagn tic behaviour (Fig. 10).

In the case of $K_3Fe((N)_6$ the formation of cementite (Fe_3C) type compounds and further reduction to iron metal starts at about 400°C. Our spectrum at 500°C heated sample, besides a parabolic distortion, tallies very closely to the spectrum reported for cast iron superimposed by paramagnetic and ferromagnetic form of cementite (see Ref. 14 Fig. 11), The spectrum of 650°C heated sample is to a great extent, of iron metal with still remaining portions of Fe_3C type compounds. Here it may be noted that the formation of Fe_5C_2 type compounds[15] may also be expected in view of the interstitial nature[17] of cementite compounds.

The formation of Fe_2O_3 in the case of Rb complex, which is otherwise anhydrous and should, likewise K complex, give Fe as the end product, may be explained due to some tightly bound interstitial water.

A difference was also observed in the Mössbauer spectra of heated Na complex in the two types of heating processes (compare the spectra at low temperatures heating in Fig. 1 end 3). No detectable difference in the case of other complexes was observed. In the case of Na complex the spectra of 100 and 150°C furnace-heating show a broadening of the original doublet plus a narrow doublet probably due to anhydrous complex formation. The absence of such component in capsule heating may be explained by assuming that the ejected vapour is reabsorbed when cooled down to room temperature (in the case of furnace the water vapour is pumped out by the vacuum pump) or water from at-

mosphere is absorbed in the process of preparing the absorber samples, as the complex is very hygroscopic. Some hydro-pressure effects in the capsule heating may also be present. The latter suggestion is born out in observing that the decomposition of prepared sodium aquopentacyanoferrate(III), was much quicker and complete at relatively lower temperature in case of glass capsule heating as compared to the furnace heating, where continuously vacuum pump was kept on (see Fig. 9c and d).

In general, observed pressure effects viz., changing of Fe^{3+} to Fe^{2+} and Fe^{II} to Fe^{2+} are reversible but irreversible effects are also observed (18). In our case the end products being more stable may account this irreversibility. Thus one should note the heating conditions when comparing two results at the same temperature.

In conclusion, the presence of water plays an important role in the thermal decomposition process and the formation of end products. Further, our interpretations are compatible with the reported DTA and DGE results[8].

ACKNOWLEDGEMENTS

FIGURE CAPTIONS

Fig. 1 - Room temperature Mössbauer spectra of glass-capsule heated Na-ferri-cyanide.

Fig. 2 - Room temperature Mössbauer spectra of glass-capsule heated K-ferri-cyanide.

Fig. 3 - Room temperature Mössbauer spectra of vacuum furnace heated Na-ferri-cyanide. Note the difference in velocity scale in Fig.(a) and (b).

Fig. 4 - Room temperature Mössbauer spectra of vacuum furnace heated K-ferri-cyanide. Note the difference in velocity scale in Fig.(a) and (b).

Fig. 5 - Room temperature Mössbauer spectra of vacuum furnace heated Li-ferri-cyanide. Note the difference in velocity scale in Fig.(a) and (b).

Fig. 6 - Room temperature Mössbauer spectra of vacuum furnace heated Rb-ferri-cyanide. Note the difference in velocity scale in Fig.(a) and (b).

Fig. 7 - Room temperature Mössbauer spectra of

(a) Non heated K - ferricyanide

(b) K - ferricyanide, moist and heated at $170^{\circ}C$

(c) Na - ferricyanide kept under vacuum pump for long time and then heated at $108^{\circ}C$.

(d) Na - ferricyanide heated at $108^{\circ}C$ for the same time as in C.

Fig. 8 - Room temperature Mössbauer spectra of

(a) Non heated Na - ferricyanide

(b) $220^{\circ}C$ heated Na - ferricyanide

(c) Dimethyleamide soluble part of (b)

(d) Dimethyleamide insoluble part of (b)

(e) Non heated Na - ferrocyanide

Fig. 9 - Room temperature Mössbauer spectra of

(a) Non heated sodium aquopentacyanide complex

(b) Heated at $100^{O}C$ in glass capsule

(c) Heated at $145^{O}C$ in glass capsule
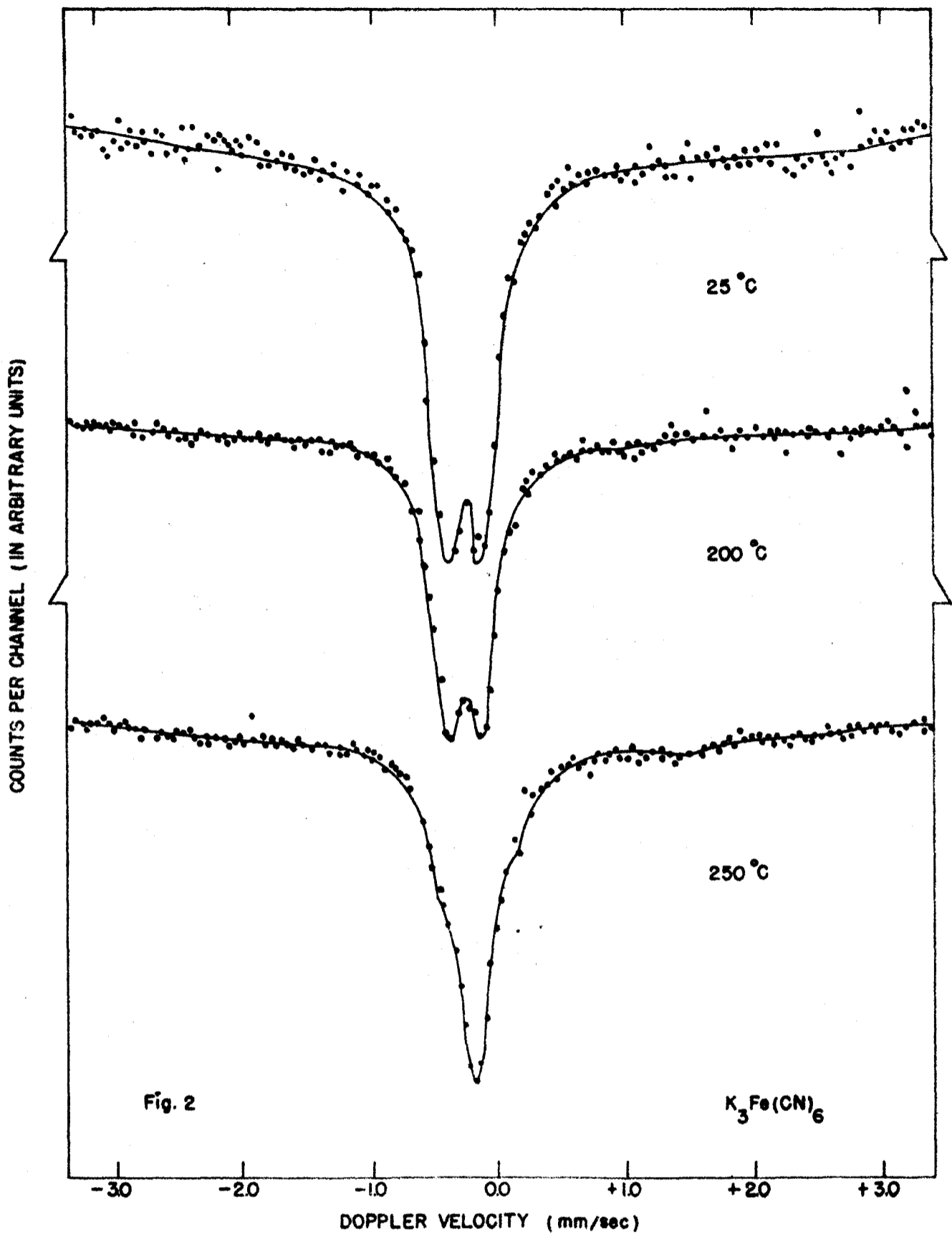
(d) Heated at $200^{O}C$ in vacuum furnace

Fig.10 - Magnetization vs applied magnetic field in the case of end   product of Li - ferricyanide heated first-directly at $520^{O}C$ and then $620^{O}C$, showing superparamagnetic behaviour.

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347a

Fig. 1   Na$_3$Fe(CN)$_6 \cdot$H$_2$O

25 °C

110 °C

155 °C

COUNTS PER CHANNEL (IN ARBITRARY UNITS)

DOPPLER VELOCITY (mm/sec)

Fig. 2

$K_3Fe(CN)_6$

25 °C

200 °C

250 °C

COUNTS PER CHANNEL (IN ARBITRARY UNITS)
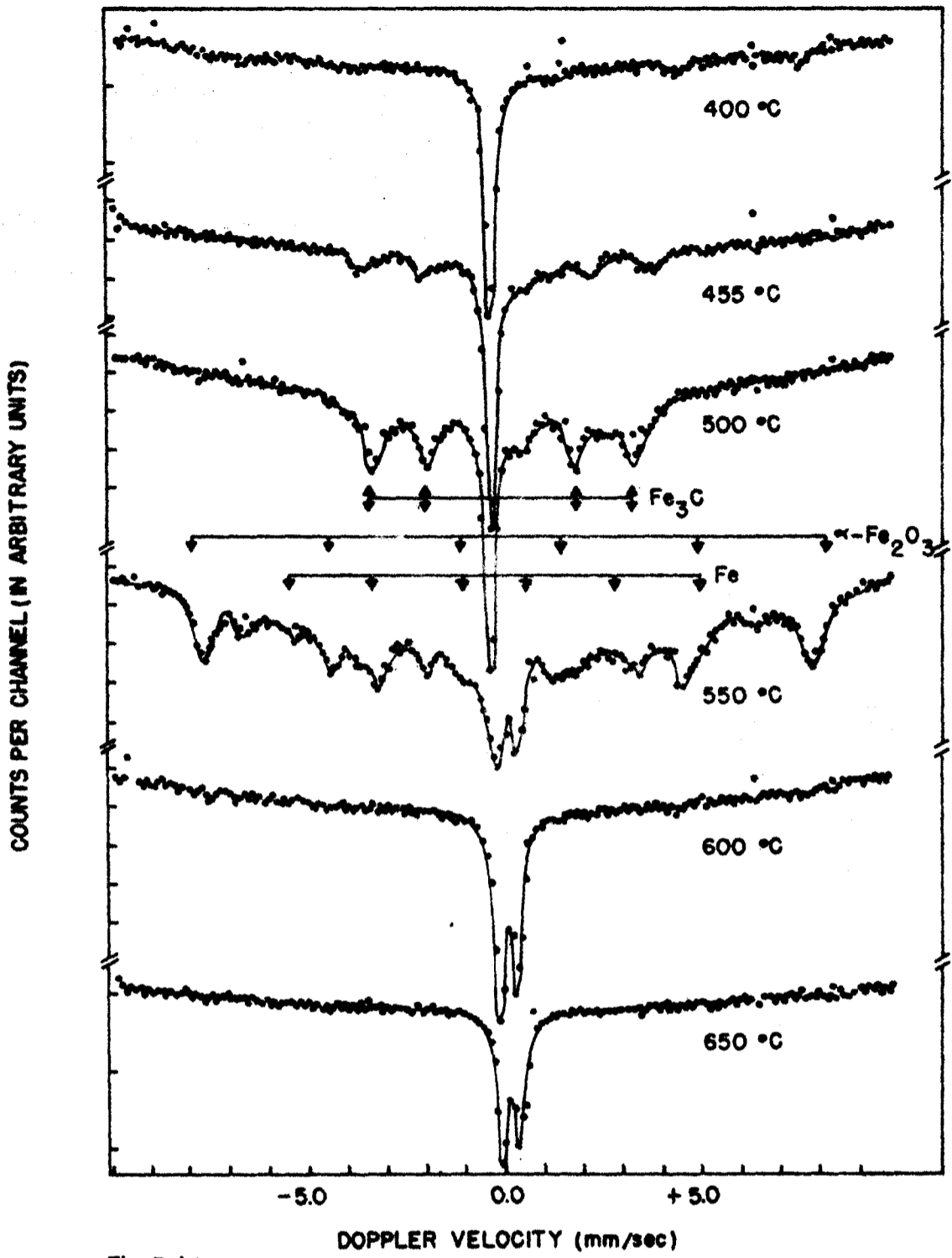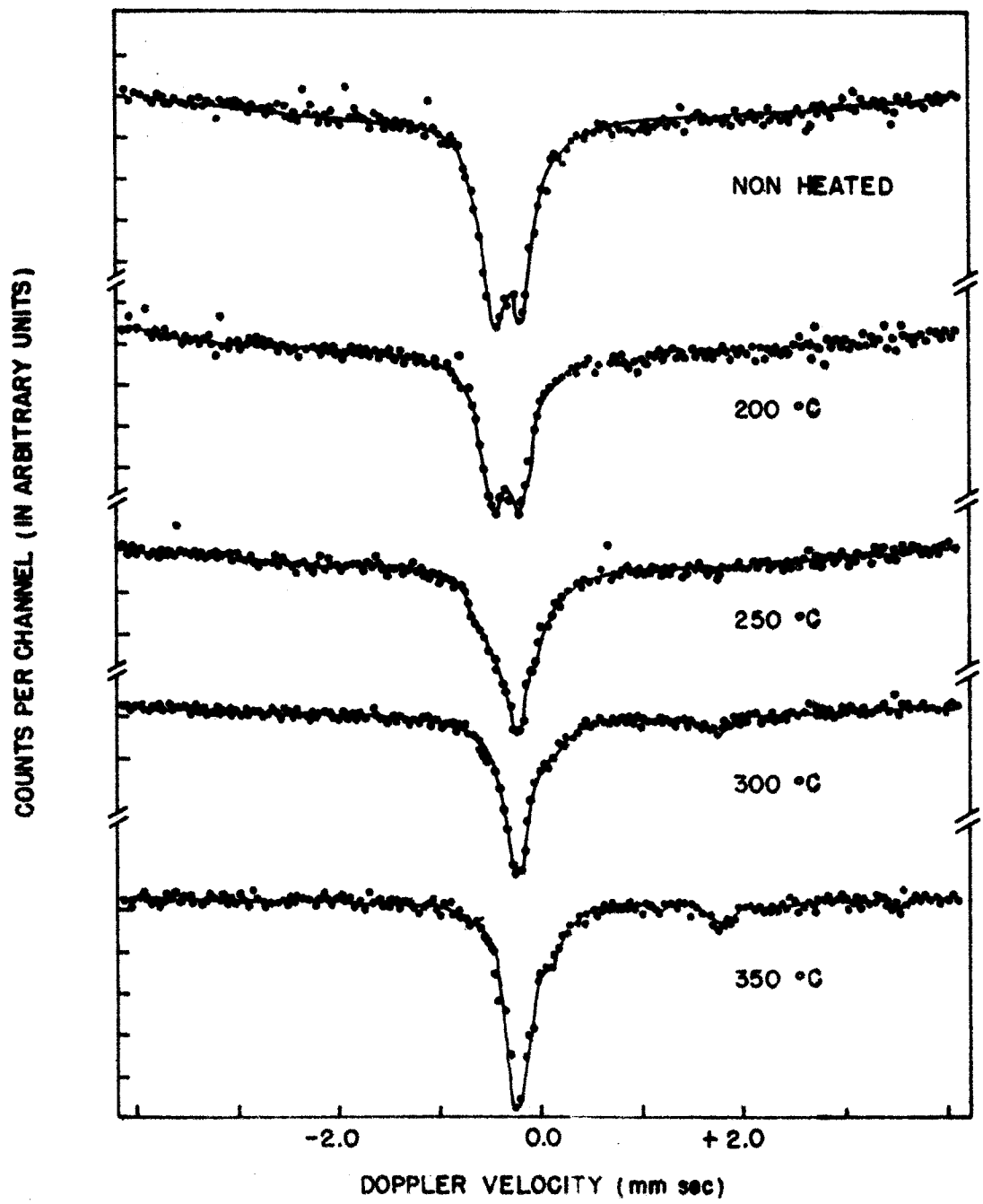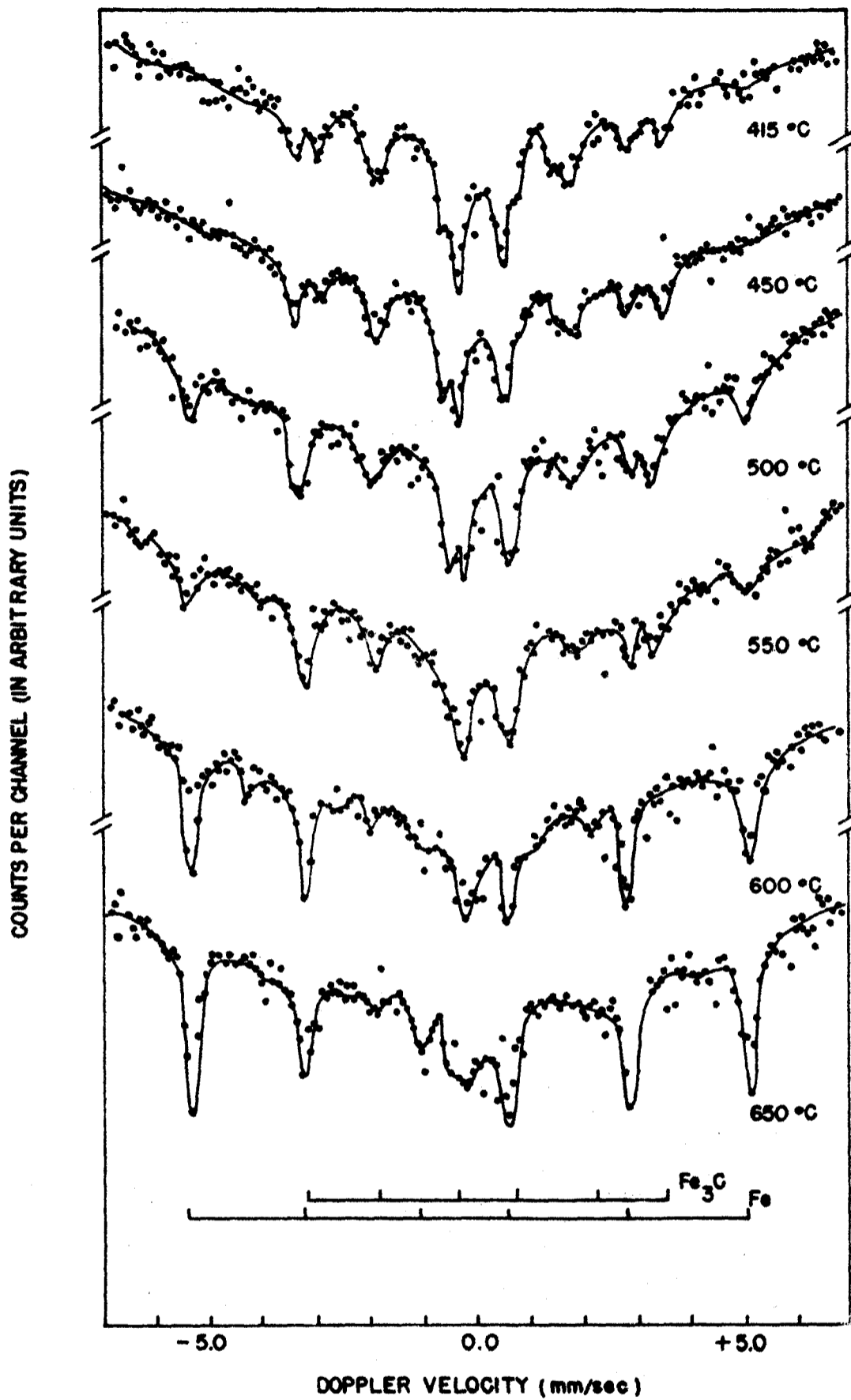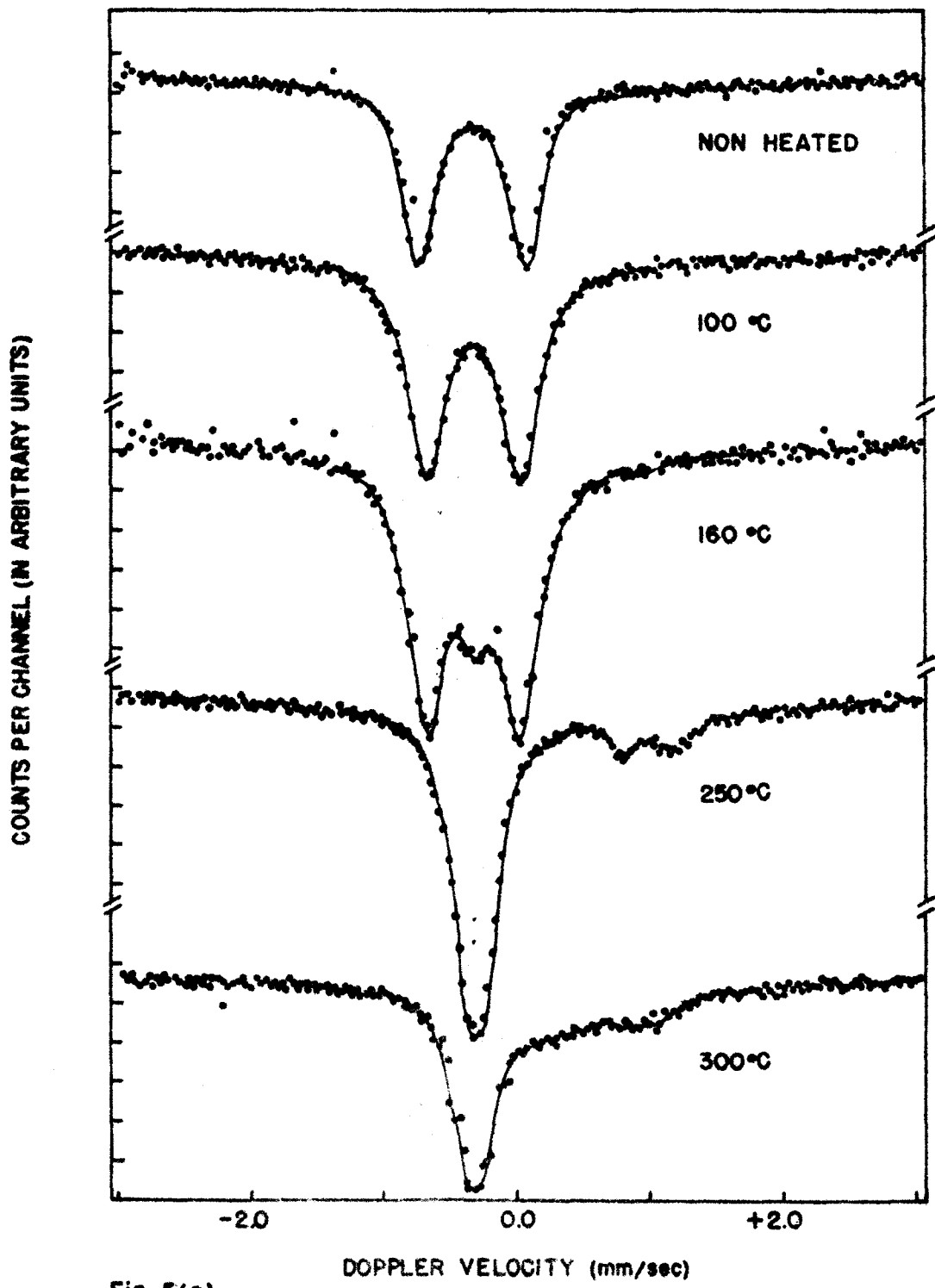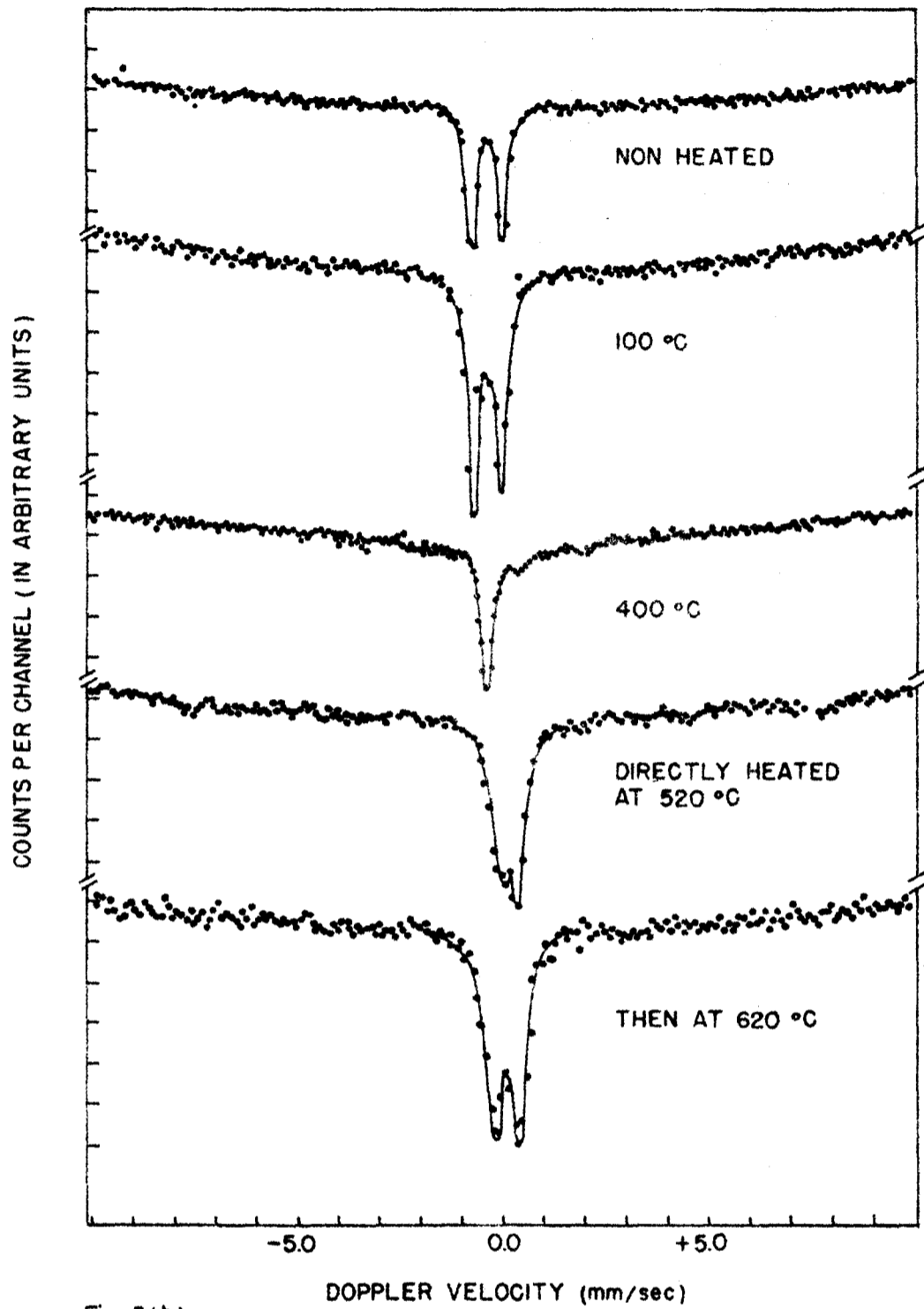
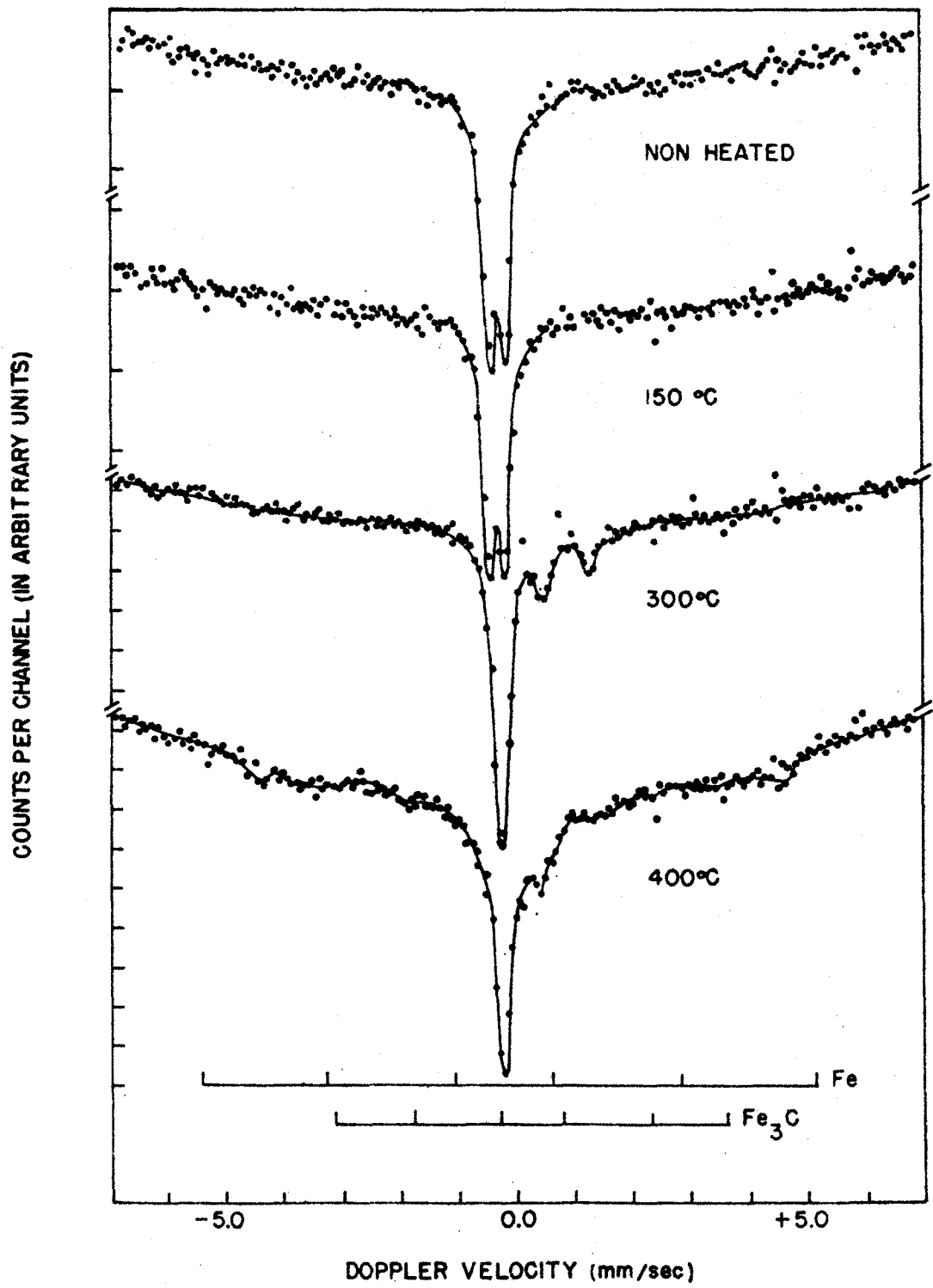DOPPLER VELOCITY (mm/sec)

Fig. 3(a)

347d

Fig. 3(b)

Fig. 4(a)
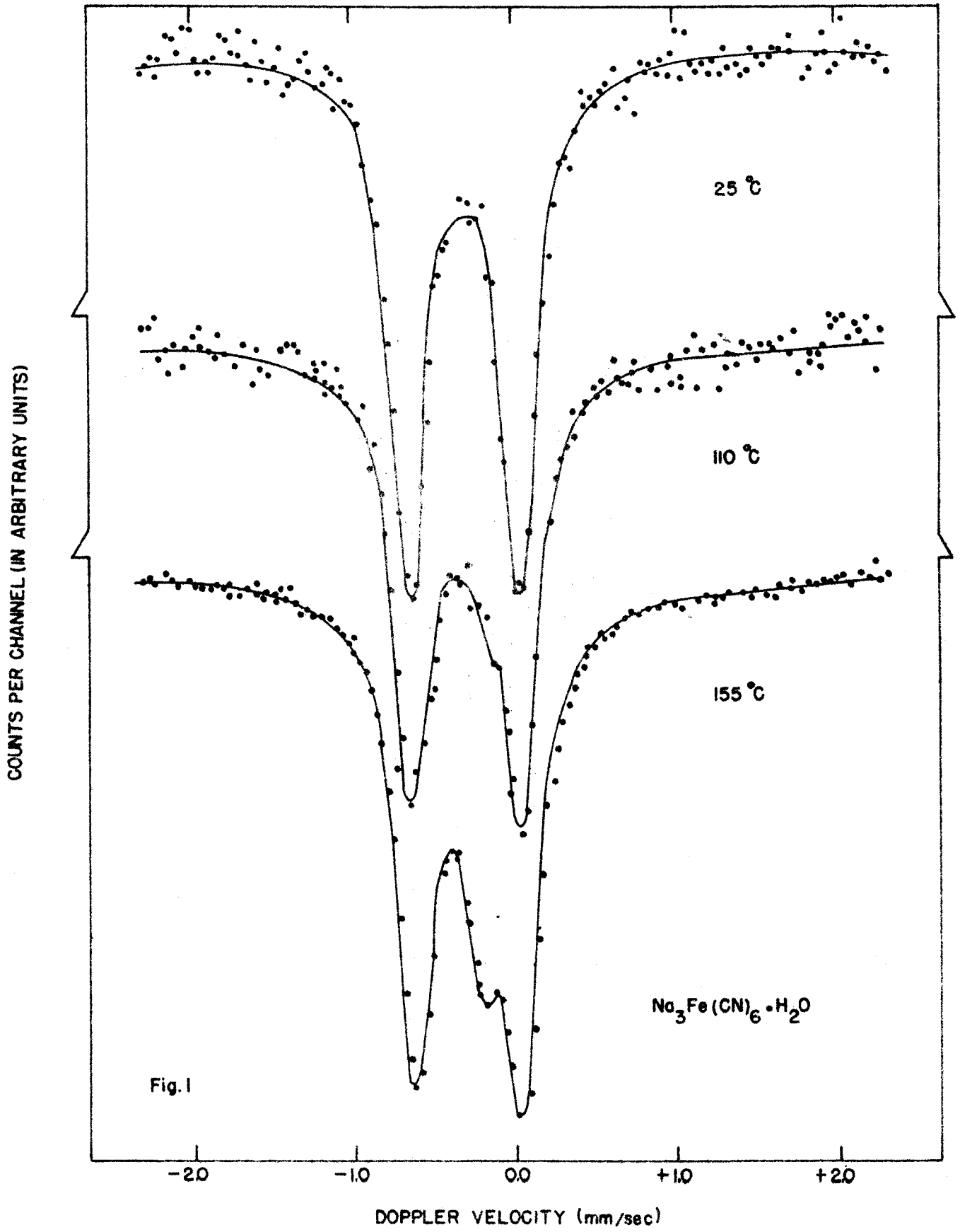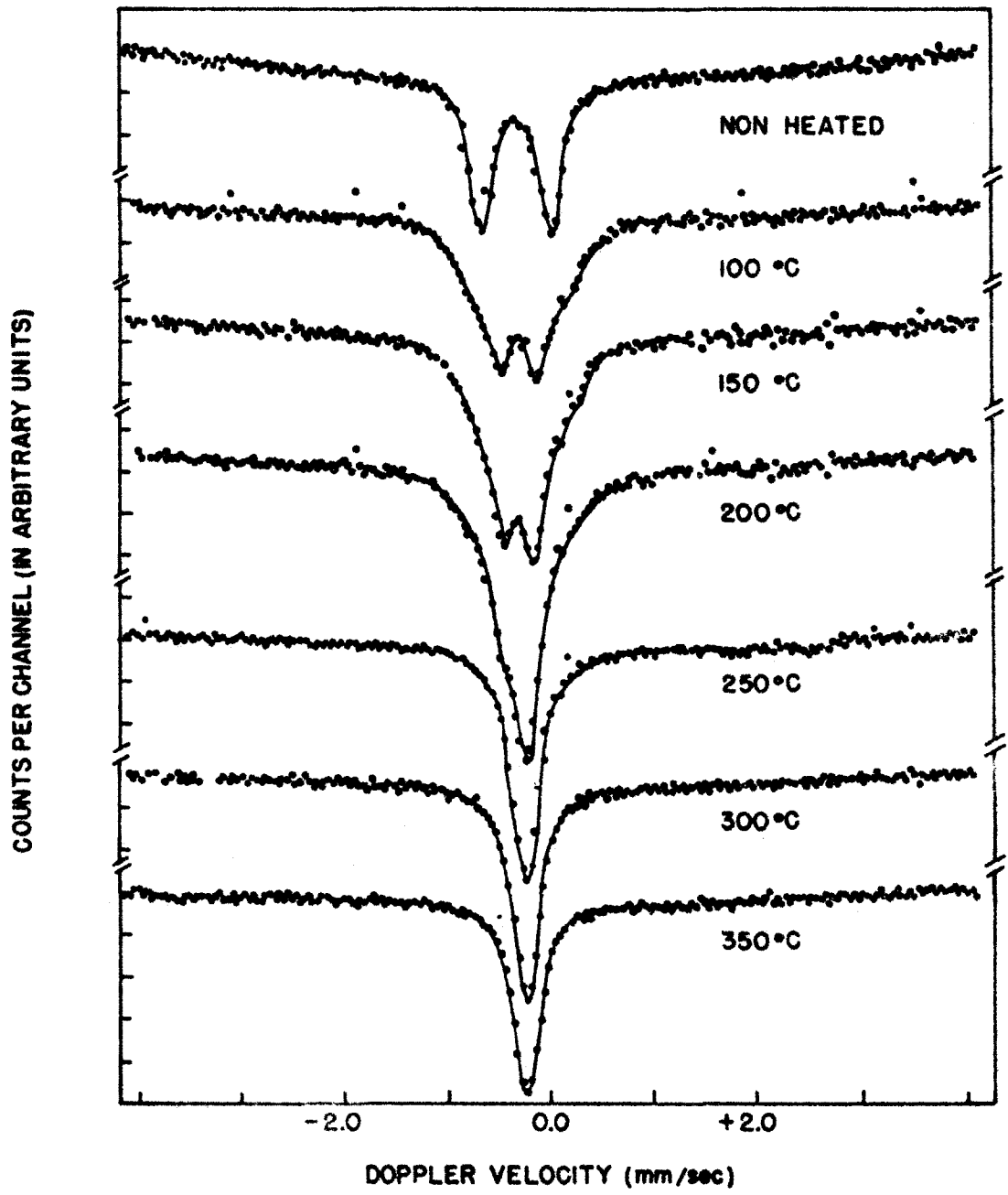
Fig. 4 (b)

Fig. 5(a)

Fig. 5(b)

Fig. 6(a)
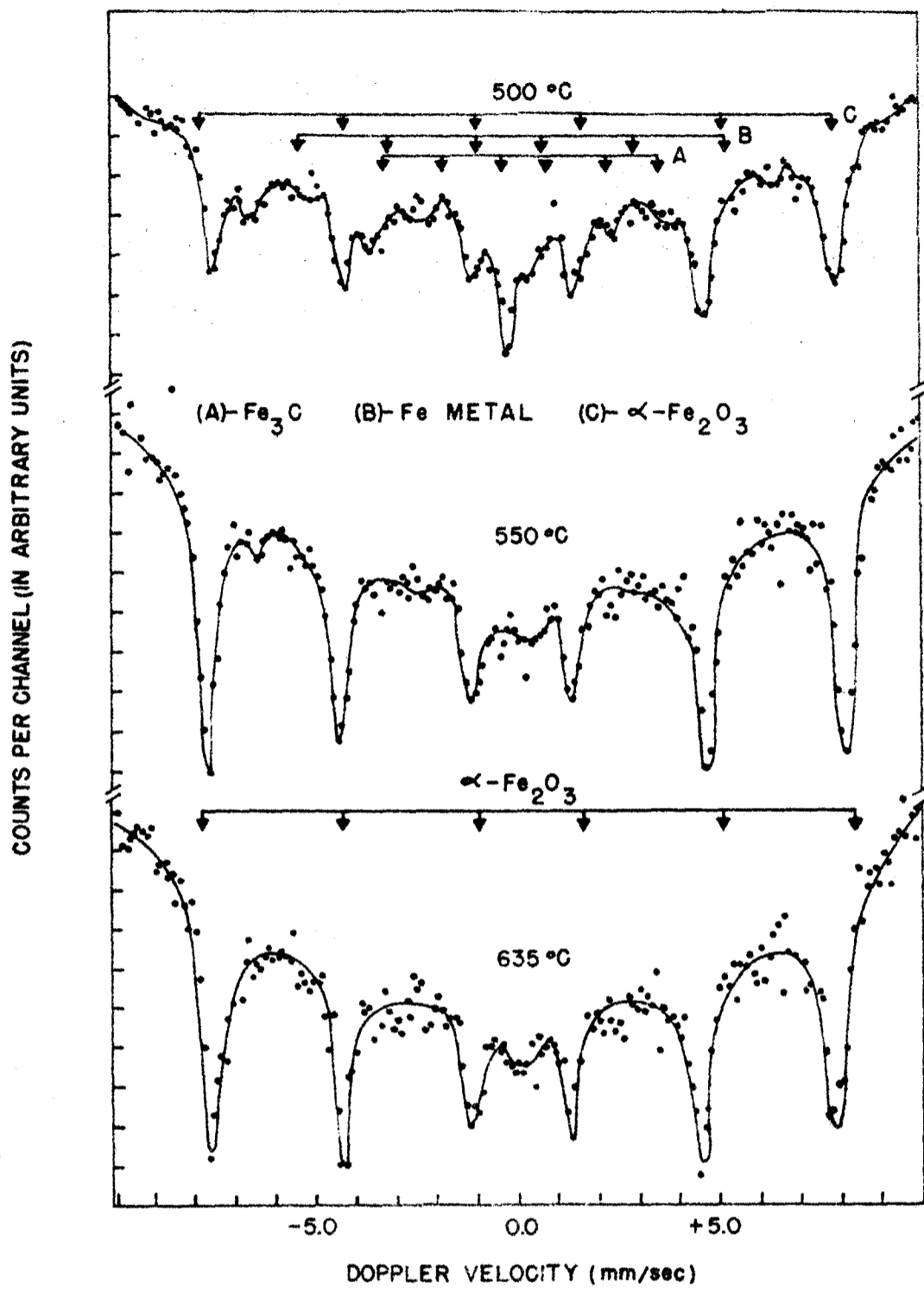
Fig. 6 (b)

Fig. 8

Fig. 9

Fig. 10