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MOTIONAL EFFECTS IN THE MÖSSBAUER SPECTRA OF IRON(II) HEXAMMINES

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In iron(II) hexammine chloride, the ferrous ion is in a high spin state [1] and each iron ion is surrounded by a regular octahedral arrangment of six NH_3 ligands. The crystal system is face centered cubic, of the type C_1 [2].

The Mössbauer spectra of this compound present a single line at room temperature, characteristic of a perfectly octahedral environment, with an isomer shift value typical of a high spin ferrous ion (figure 1). Upon cooling, two other lines, symetrical about the previous one, appear at 109,5°K; at 107°K the single line disappears and there only remains a well resolved quadrupole split spectrum. The sharpness of the transition (figure 2) leaves no doubt that we are dealing with a critical phenomenum. Moreover, upon heating, the middle line reappers only at 110°K, and is present alone above 116°K, showing that the transition exhibits an hysteresis like behaviour.

The isomer shift of the single line (1.12 ± 0.03 mm/s at 295°K) and of the quadrupole split doublet (1.24 ± 0.04 mm/s at 77°K) shows that the ferrous ions remain in the same spin state over the whole temperature range.

The appearance of a well resolved quadrupole splittling at low temperature shows that the cubic symmetry at the iron sites is not maintained below a critical temperature T_c. The most probable explanation for this phenomenum can be given on the basis of analogous results observed in the EPR spectra of the isomorphous nickel(II) hexammine halides.[3]

The EPR spectra of these complexes show an abrupt line-with increase with decreasing temperature, which has been interpreted as due to a critical transition from cubic to trigonal symmetry, induced by the variable rotation frequency of the ligand molecules [3, 4].

The same explanation applies for the Mössbauer spectra of iron(II) hexammines. Bates and Stevens [4] showed that there exist several equivalent preferred static arrangments of the six groups of H_3 protons associated with one metal haxammine cluster, each possessing trigonal symmetry. One goes from one stable H_3 triangle to another by rotation around the metal nitrogen axes.

At high temperature, the ferrous ions are in a cubic symmetry ligand field. However, the $Fe(NH_3)_6$ clusters cannot present cubic symmetry unless the NH_3 ligands rotate fast enough (as compared with the nuclear quadrupole precession frequency) around the metal nitrogen axes, so that the crystal field symmetry corresponds to an average of their motion.

Because of a cooperative interaction between neighbouring clusters, the NH_3 ligands get frozen below a critical temperature T_c into the preferred arrangments, which always provide the same trigonal symmetry. A well resolved quadrupole splitting is observed when the frequency of rotation between these energetically favoured positions becomes lower than the quadrupole precession frequency $\omega_Q \simeq \frac{\Delta E_Q}{\hbar} = (1.75 \times 10^9\ s^{-1})$. The degeneracy of the t_{2g} sub level of Fe^{+2} is then lifted into a singlet and a doublet. Such a situation involves an electric field gradient at the iron nucleus. It is found that the resulting quadrupole splitting varies linearly with temperature in the range investigated: $\varepsilon(mm/s) = 2.07 - 0.0058 \times T$.

The observed hysteresis is not unexpected because it concerns a cooperative order-disorder modification between neighbouring clusters. In fact, a similar hysteresis phenomenum has been observed in dilatometric [5] and EPR [6] investigations of the nickel(II) hexammines.

Similar phenomena has been observed in the Mössbauer spectra of ^{57}Fe doped $Co(NH_3)_6\,Cl_2$ and of ^{57}Co $Co(NH_3)_6\,Cl_2$ sources [7].

Experiments are in progress with the heavier halides $Fe(NH_3)_6\ Br_2$ and $Fe(NH_3)_6\ I_2$ and other salts of these ammines, as well as with deuterated compounds.

EXPERIMENTAL

The light blue hexammine iron(II) dichloride was precipitated out in an air free atmosphere by passing a current of gaseous NH_3 through a solution of $FeCl_2\ 6H_2\ O$ which was prepared under hydrogen atmosphere. The complex was dried under a stream of gaseous anhydrous NH_3 [8]. It was extremely sensitive to air and moisture, and, upon exposure, immediately adopted a brownish red color. All handlings of the product were done in an atmosphere of anhydrous NH_3; the Mössbauer absorber was enclosed in tight copper capsules with Berryllium windows.

The Mössbauer spectrometer was a constant acceleration device described earlier. The least square fitting of the spectra was done using the IBM 360-65 computer of the Centres de Recherches Nucleaires in Strasbourg.

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FIGURE CAPTIONS:

Fig. 1: Mőssbauer spectra of $Fe(NH_3)_6\ Cl_2$ at 295, 109 and 99°K.

Fig. 2: Percentage of the intensity of the quadrupole split line against temperature. The arrows indicate the direction of temperature variation.

REFERENCES:

1. A. Earnshaw, Introduction to magnetochemistry, Acad. Press, New York (1968).

2. G. Bodker-Naess and O. Hassel, Strukturberichte III (1933), p. 475. L. Sacconi, A. Sabatini and P. Gans, Inorg. Chem. 3, 1773 (1964).

3. T. Garofano, M. B. Palma-Vitorelli, M. U. Palma and F. Persico, Proc. Int. Conf. on Paramagnetic Resonance, W. Low edit. (1962), Vol. II, p. 582.

4. A. R. Bates and K. W. H. Stevens, J. Phys. C. 2, 1573 (1969).

5. D. G. Thomas, L. A. K. Staveley and A. F. Cullis, J. Chem. Soc. 1727 (1952).

6. C. E. Hennies, Thesis University of São Paulo (1969).

7. J. M. Friedt, A. Cruset and J. P. Adloff (to be published).

8. Inorganic synthesis, p. 161. vol. IV.

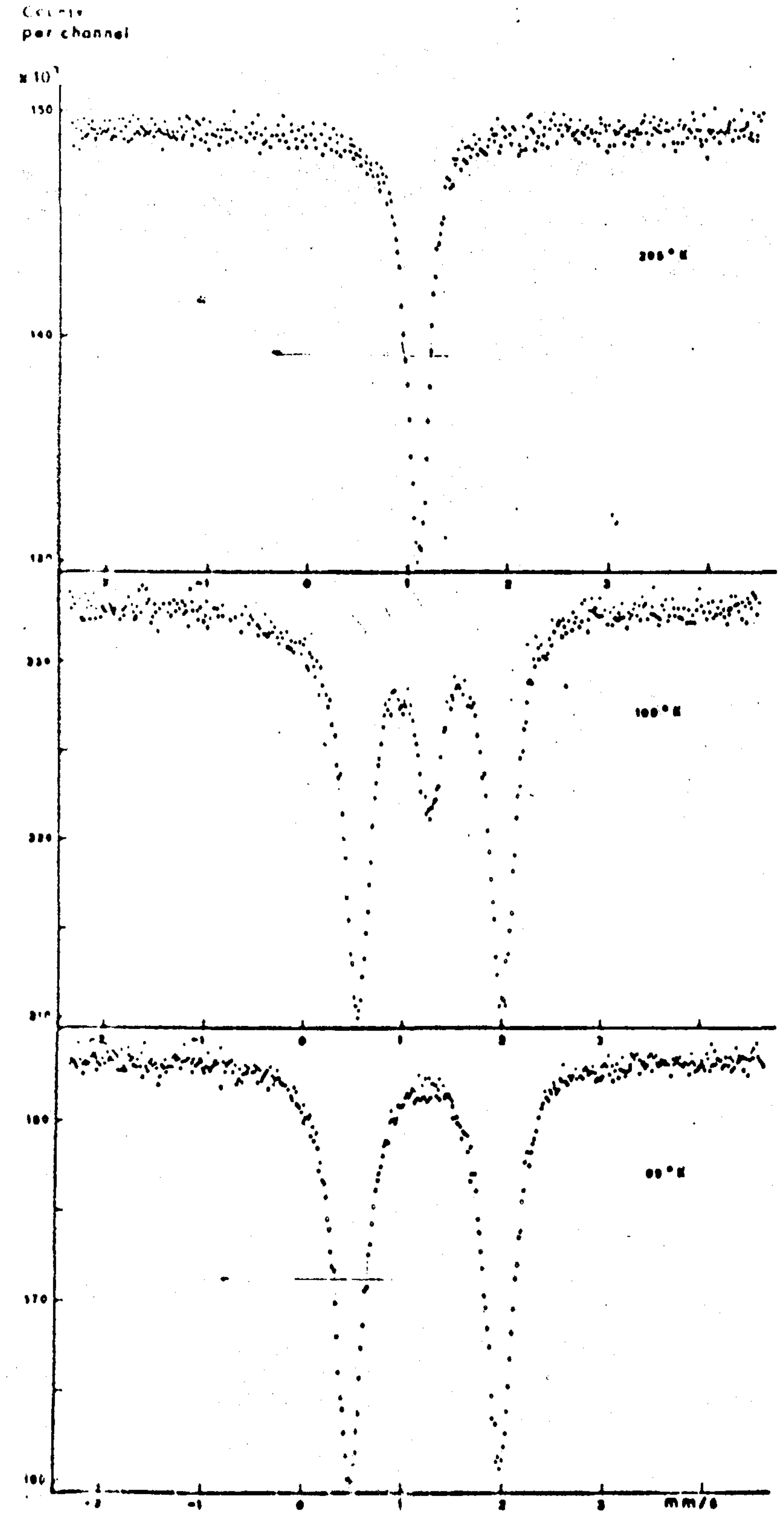

FIG. 1

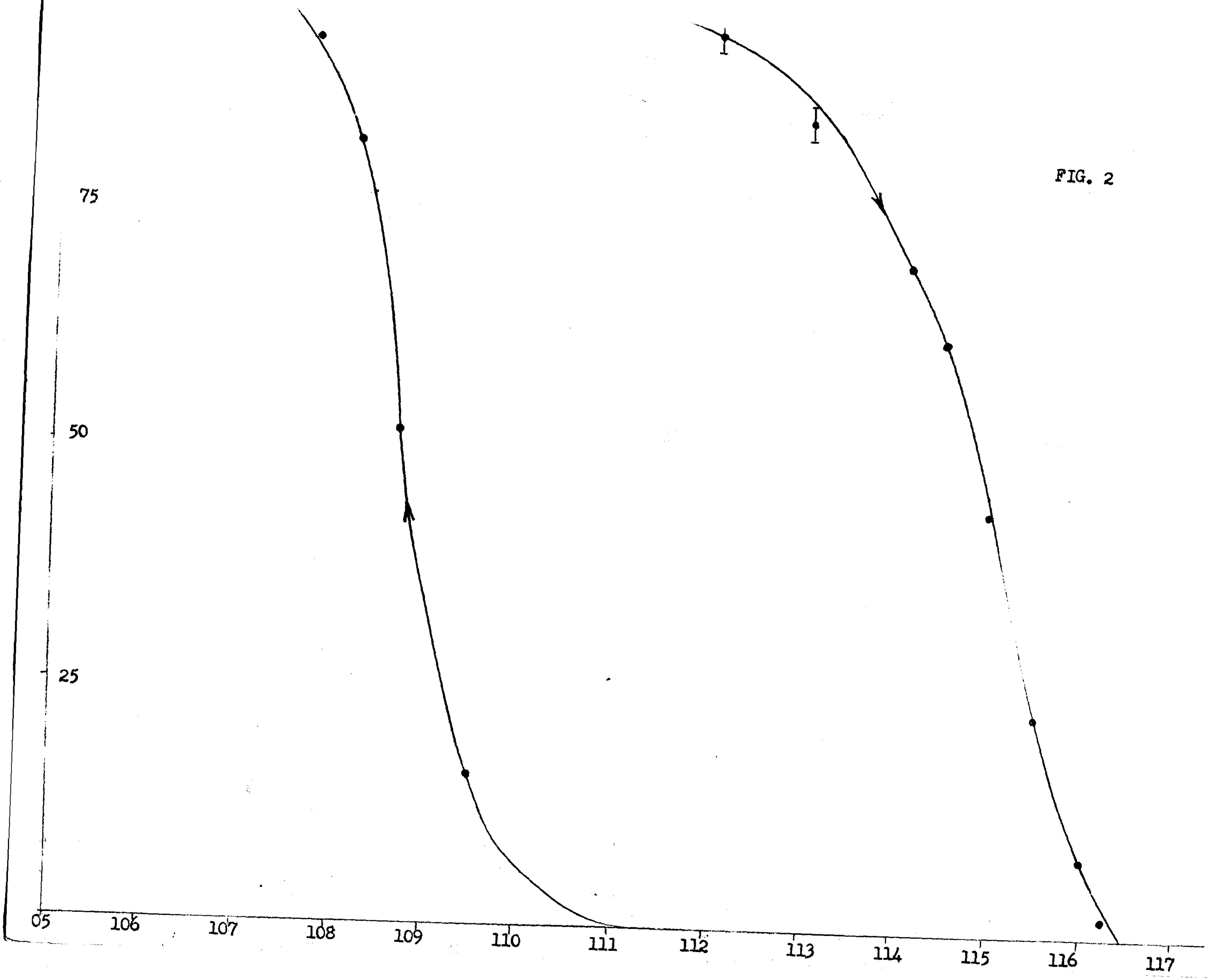

FIG. 2