MÖSSBAUER EFFECT OF IRON IN

ANHYDROUS COBALTOUS   CHLORIDE

by

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ABSTRACT

The Mössbauer spectra of $^{57}Co-CoCl_2$ reveal ^{57}Fe in
the +2 charge state. Isomer shift and quadrupole
splitting are discussed. An interpretation is   sug-
gested for the observation of only the ferrous ionic
state.

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We report in this paper precision measurements of the Möss-bauer spectra of ^{57}Co doped anhydrous $CoCl_2$ sources, between 80 and 500°K [1]. The main purpose of the work was to get further insight in the formation process of multiple charge states after the electronic capture of ^{57}Co.

$CoCl_2$ presents rhomboedral structure, of type $CdCl_2$ (space group D_{3d}-3m). The Co^{+2} ions stay in a nearly octahedral environment of $6Cl^-$ anions, distorted along its trigonal (1,1,1) axe, which corresponds to the crystal c axe. Cations and anions are arranged in hexagonal layers perpendicular to the c axe, with the Co^{+2} layers beeing separated by two layers of Cl^- anions.

EXPERIMENTAL

The Mössbauer spectrometer was of constant acceleration type. The moving ^{57}Fe enriched ferrocyanide absorber was kept at room temperature. The ^{57}Co-$CoCl_2$ source was prepared by evaporation of a solution of $CoCl_2$ containing 0.5 to 1 mci of ^{57}Co, followed by carefull drying under HCl or N_2 atmosphere at 180°C. Special precautions were taken against rehydratation of the salt during the experiments. The Mössbauer parameters were obtained by a least square computer curve fitting, supposing that individual lines present theretical Lorentzian line shape.

EXPERIMENTAL RESULTS

The Mössbauer spectra of ^{57}Co-CoCl$_2$ (figure) present two peaks of inequal heights and same linewidths. The isomer shift characterises ferrous ions; the quadrupole splitting is unusually low (typical values of ε for Fe^{+2} range from 2 to 3.5 mm/s) and strongly temperature dependant (Table). These features are however well in agreement with Mössbauer measurements of absorbers of ferrous halides [2].

T	$-\sigma$	ε	Γ	h_1/h_2
95	1.27	1.02	0.41	1.06
295	1.14	0.92	0.38	1.11
375	1.05	0.81	0.37	1.19
470	1.00	0.69	0.45	1.23

Table: Mössbauer parameters of ^{57}Co doped CoCl$_2$ source. Temperature in °K, isomer shift: σ against Na$_4$Fe(CN)$_6$, 10H$_2$O, quadrupole splitting: ε and linewidth: Γ all in mm/s. h_1/h_2 is the ratio of the intensities of the two lines. The error upon σ, ε, and Γ is 0,03 mm/s.

DISCUSSION OF THE EXPERIMENTAL RESULTS

The isomer shift of the ferrous ions formed after electronic capture of cobalt 57 in CoCl$_2$ is higher than in ferrous chloride. This is attributed to a stronger delocalisation of the 3d electrons, which might be induced by a pressure effect. (The ionic radius of Fe^{+2} is larger than that of Co^{+2}) or be caused by an incomplete lattice rearrangement after the nuclear
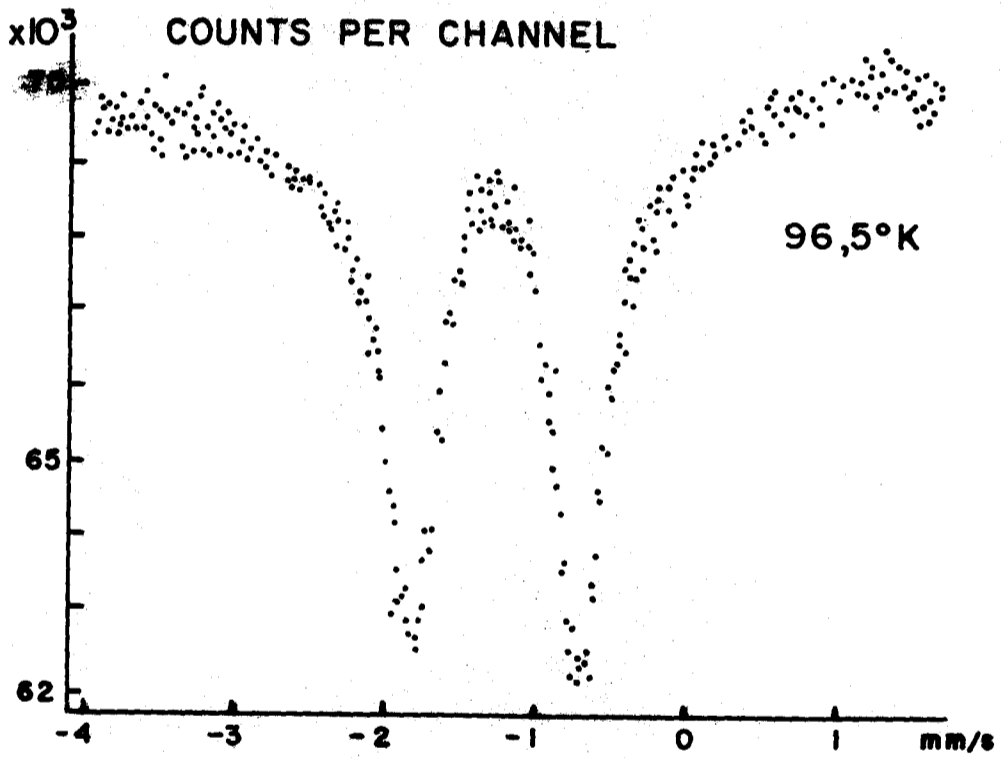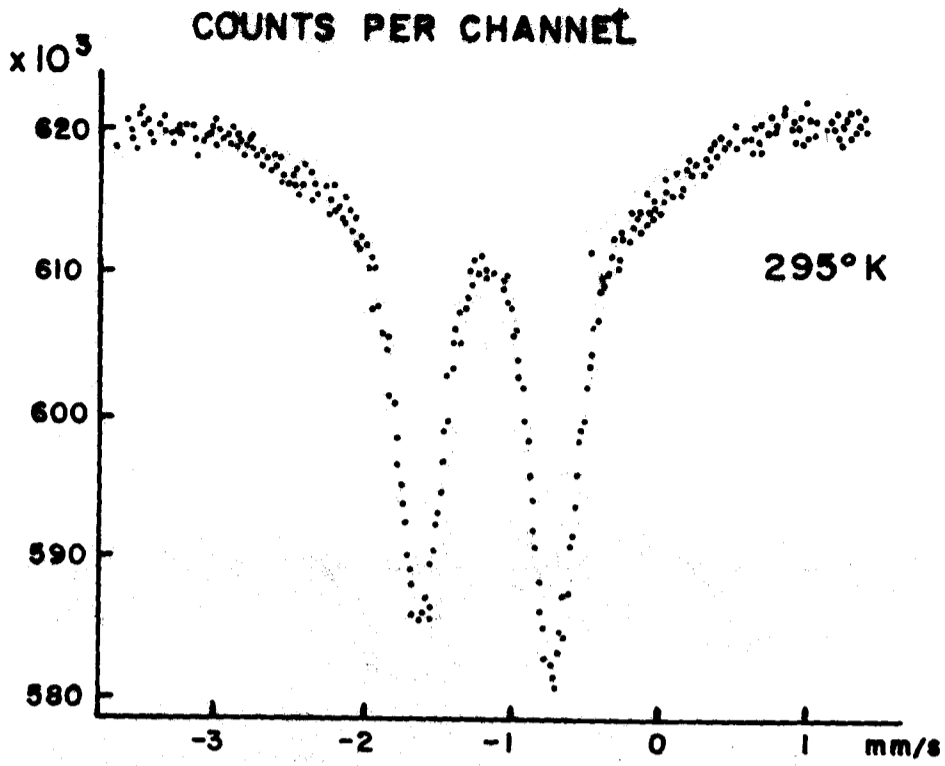
Mössbauer spectra of ^{57}Co-$CoCl_2$

event. It has already been noticed that the isomer shifts of the ions thus formed by ^{57}Co E. C. always imply a higher ionicity of the bonding than in the corresponding iron compounds [3]. The temperature variation is due to the second order Doppler shift $(6 \times 10^{-4} \text{ mm/s/°K})$.

The quadrupole splitting is well described using earlier theoretical works by Ingalls and Gibb [4]. In the case of ^{57}Fe-CoCl$_2$, the crystal field perturbation hamiltonian acting upon the ^{5}D state is written:

$$V = V_{cubic} + V_{trigonal} = C_4(x^4 + y^4 + z^4 - \frac{3}{5} r^4) + B_2^0 (3z^2 - r^2)$$

The cubic term splits the ^{5}D state into an orbital doublet $d\gamma$ and a triplet $d\epsilon$, whose energy separation is about 7000 cm^{-1} at 295°K [5]. The three-fold degeneracy of the $d\epsilon$ lower state is lifted by the trigonal field and the spin orbit interaction, whose effects are described by the equivalent operator hamiltonian $- \lambda \hat{L} \hat{S} - \frac{\Delta_t}{3} (3 \hat{L}_z^2 - \hat{L}^2)$ acting upon the wave functions

$$\frac{2}{3} \psi_{-2} + \frac{1}{3} \psi_1$$
$$\psi_0$$
$$\frac{1}{3} \psi_{-1} - \frac{2}{3} \psi_{-2} .$$

The 15 × 15 perturbation matrix has been solved by several authors [4]. It may be concluded from the small value of ϵ and from a comparison with isomorphous FeCl$_2$ experiments that Δ_t is positive.

Only q_{zz} contributes to the quadrupolar interaction since the crystal field presents axial symmetry. As the thermal transition frequencies between the sublevels are much higher that the quadrupole precession frequency ($\underset{\sim}{} 10^9$ s^{-1}), the principal component of the electric field gradient is an average over the electronic states:

$$q_{zz} = \frac{\sum_n (q_{zz})_n \ e^{-\mathcal{E}_n/kT}}{\sum_n e^{-\mathcal{E}_n/kT}}$$

where $(q_{zz})_n = \frac{4}{7} e \langle r^{-3} \rangle \langle \phi_n | 3 \hat{\ell}_3^2 - \hat{\ell}^2 | \phi_n \rangle$ and ϕ_n is the eigenvector of the nth eigenstate with energy $\mathcal{E}_n$. Neglecting the lattice contribution, the quadrupole splitting is then written in terms of a dimensionless factor F which is a function of Δ_t and λ:

$$\mathcal{E} = \frac{e \ q_{zz} \ Q}{2} = \frac{2}{7} e^2 \ Q(1-R) \alpha^2 \ \langle r_o^{-3} \rangle \ f(\Delta_t, \alpha^2 \lambda_o, T)$$

where Q is the quadrupole moment of the first excited nuclear state, R the Sternheimer polarization factor ($+ 0.32$), $\alpha^2 = \frac{\lambda}{\lambda_o}$ the covalency factor accounting for the reduction of the spin orbit coupling constant λ and $\langle r^{-3} \rangle$ from the free ion values λ_o (103 cm^{-1}) and $\langle r_o^{-3} \rangle$ (4.8 a.u.).

Using Ingalls estimate for Q (0,29 barn) it is found that $\mathcal{E} = 5.62 \ \alpha^2 \ F(\Delta_t, \alpha^2 \lambda_o, T)$. We supposed that the λ value is the same as in $FeCl_2$: 95 cm^{-1} (2) and found $\Delta_t = 160$ cm^{-1} with the help of the graphical results from reference 4.

However, the value of Q is not yet definetely established. Using Q = 0,18 barns and the same values for the other parameters, it is found that Δ_t = 285 cm^{-1}. The values of Δ_t deduced from Mössbauer spectra are thus rather imprecise.

Furthermore, as is indicated by the isomer shift value, the spin orbit coupling constant should probably be somewhat higher for $^{57}Fe^{+2}$ in $CoCl_2$ than in $FeCl_2$, and the value of λ proposed in several works for Fe^{+2} in $FeCl_2$ (2) seems to be anomalously high considering the covalency of the bonding. The main point is that the small value of the quadrupole interaction energy and its strong temperature dependance may well be explained by a strong mixing of the different electronic states under influence of the crystal field and spin orbit coupling and a small energy gap between the lowest levels.

The slight inequality of the peak heights of the spectra of Fe^{+2} formed in $CoCl_2$ is attributed to an anisotropy of the Lamb Mössbauer factor [7], in accordance with the layer structure of the compound. Relaxation effects and preferred orientation of the microcrystals were ruled out respectively by considering that both peaks have the same linewidth and that their intensity ratio does not vary with the orientation of the source relative to the γ ray axe. The increase of the spectra asymetry with temperature is expected for the Goldanskii-Karyagin effect, which is invoked here.

CHARGE STATES OF ^{57}Fe AFTER ELECTRON CAPTURE IN ^{57}Co

The interesting fact is that ^{57}Fe is only found in the fer-vous state in anhydrous $CoCl_2$. The difference against the hydrates of cobaltous chloride has already been discussed, and the appearance of ferric ions in the hydrates has been attributed to radiochemical reactions following the local autoradiolysis [8].

Whereas only Fe^{+2} is observed in $CoCl_2$, the presence of Fe^{+2} and Fe^{+3} has been detected in CoF_2 [6]. The appearance of ferric ions in the CoF_2 lattice may be related to the increase of the lattice energy and of the Madelung constant on going from $CoCl_2$ to CoF_2. Similar correlation has already been found in the complex fluorides $KCoF_3$ and K_3CoF_6 (3). This qualitative rela-tion could mean that the higher charge states of ^{57}Fe may be observed if the local variation of electrostatic energy associated with the change of charge is high enough against the ionization potential of the normal charge state of iron. This variation of electrostatic energy is of course related to the Madelung constant of the lattice. Calculations are under work to verify these hypo-theses in several type of compounds.

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