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HYPERFINE INTERACTIONS AND COVALENCY
IN INSULATORS.

HYPERFINE INTERACTION OF THE Fe$^{2+}$ ION IN Fe(H$_2$O)$_6$.(ClO$_4$)$_2$

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Abstract. — Mössbauer spectra of Fe(H$_2$O)$_6$. (ClO$_4$)$_2$ have been measured at 4.2 K in longitudinal external magnetic fields up to 50 kG and fitted in the ligand field (T$_{2g}$) approximation. The symmetry of the ligand field is mainly D$_{3h}$ with a small distortion D$_{3h}$. Because of the almost identical behaviour of the Fe(H$_2$O)$_6$ molecules in the compounds ferrous perchlorate and ferrous fluosilicate (same isomer shift and ligand field symmetry) it is assumed that the covalency and hyperfine constants are the same too. The attempt to fit the Fe(H$_2$O)$_6$. (ClO$_4$)$_2$ spectra with the known parameters of ferrous fluosilicate has been successful. Moreover, it can be differentiated between the covalency of the orbital states ($\lambda = 0.96$) and the radial expansion of the 3d-electron distribution via the reduction of the spin-orbit coupling constant ($\lambda = 95$ cm$^{-1}$).

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1. Introduction. — The hyperfine interaction of the high-spin Fe$^{2+}$ ions have been studied in many compounds to solve the appropriate ligand field problem. The usual methods, susceptibility and Mössbauer measurements, are not sufficient to determine the ligand field, covalency parameter and hyperfine constants uniquely. In every case some reasonable suggestions have been made to limit the number of independent parameters. Especially covalency parameters and hyperfine constants are chosen with qualitative arguments. In the present work another concept will be used.

The compounds, hexahydrated ferrousperchlorate and ferrousfluosilicate, have the following properties. The crystals are built up of the complexes Fe(H$_2$O)$_6$, ClO$_4$ and SiF$_6$, respectively. The Fe(H$_2$O)$_6$ molecules are known from Mössbauer measurements to behave similarly in both lattices at 4.2 K. First of all the isomer shifts are almost equal which indicate, following the arguments of Hazony [1], the same charge distribution of the Fe$^{2+}$ ion. Coey et al. [2] and Reiff et al. [3] have shown that the orbital ground state of ferrousperchlorate is the singlet state $d_{3g} = t_{2g}^0$ implied trigonal symmetry of the ligand field, which is the same situation in ferrousfluosilicate. The trigonal field splitting $\delta$ between the singlet $t_{2g}^0$ and the higher doublet $\{ t_{2g}^0, t_{2g}^0 \}$ of the cubic $T_{2g}$ ground state are of the same magnitude because of nearly the same quadrupole splitting at 4.2 K.

Generally Fe(H$_2$O)$_6$ molecules have similar isomer shifts [1] due to the fact that in these crystals the molecule itself determines the chemical binding to the iron atom. The small differences are caused by the different environments giving rise to different ligand fields at the iron atom. In this case the ligand field is essentially the same too, so that the whole state of the molecules can be assumed to be very similar and to result in equal covalency parameters and hyperfine constants. Therefore the conception is to fit the ligand field and hyperfine parameters of Fe(H$_2$O)$_6$ in both lattices with the additional equations obtained by equating the covalency parameter and hyperfine constants.

2. Ligand field and hyperfine parameters. — The ligand field Hamiltonian $H$ is described in terms of $C_{3h}$ symmetry parameterized in $T_{2g}$ subspace of the Fe$^{2+}$ high-spin state $^3$D. The eigenvalues are expressed as

\[ E^0 = 0, \quad E^- = \delta - a, \quad E^+ = \delta + a \]
and correspond to the orbital eigenstates
\[ \varphi^0 = \cos \theta t^0_{2_2} - \sin \theta t^+_{2_2}, \quad \varphi^- = t^-_{2_2}, \]
\[ \varphi^+ = \sin \theta t^0_{2_2} + \cos \theta t^+_{2_2}. \]
The \( t^0_{2_2} \) states are as used in [4]. The equations define two energy splittings \( \delta, a \) and one mixing angle \( \theta \). The total Hamiltonian with applied magnetic field \( \mathbf{H} \) is given by
\[ \mathbf{H} = \lambda \mathbf{L} \mathbf{S} + \mu_B (\mathbf{L} + 2 \mathbf{S}) \mathbf{H}, \]
where the orbital momentum \( \mathbf{L} \) is reduced by \( \alpha^2 \) due to a covalent mixing of the states of the free ion and the ligands. A reduction of the spin-orbit coupling constant \( \lambda \) is taken into account by a factor \( k : \lambda = k \lambda_0 \) \( (\lambda_0 = -103 \ \text{cm}^{-1}) \), which is caused by a radial expansion \( (k < 1) \) of the 3d-electron distribution. \( k = 1 \) and \( k = \alpha^2 \) will be discussed.

The effective magnetic field at the nucleus in the case of fast relaxation
\[ \mathbf{H}_{\text{eff}} = -H_L \mathbf{L} < \mathbf{L} >^T - H_S < \mathbf{S} >^T - H_{\text{sd}} < \mathbf{O}_{\text{sd}} >^T + \mathbf{H} \]
requires two parameters \( H_L = 2 \mu_B < r_{L}^{-3} > \) and the Fermi contact field \( H_S \). The constant
\[ H_{\text{sd}} = 2 \mu_B < r_{\text{sd}}^{-3} > \]
is related to the spin dipole operator \( \mathbf{O}_{\text{sd}} \). The expectation values \( < r_{L}^{-3} > \) and \( < r_{\text{sd}}^{-3} > \) are assumed to be equal.

The dependence of the EFG tensor
\[ \mathbf{V} = (1 - \gamma_0) \mathbf{V}_{\text{val}} + (1 - \gamma_0) \mathbf{V}_{\text{hst}} \]
on the magnetic field \( \mathbf{H} \) is neglected. The lattice contribution \( (1 - \gamma_0) \mathbf{V}_{\text{val}} \) is assumed to be small and proportional to \( (1 - \gamma_0) \mathbf{V}_{\text{val}} \) the EFG produced by the 3d electrons [5]. Since the quadrupole splitting
\[ \Delta E_Q = \left| \frac{e Q V_{zz}}{2} \right| \left( 1 + \frac{1}{5} \eta^2 \right) \]
is taken from the zero field spectrum and the asymmetry parameter \( \eta = (V_{xx} - V_{yy})/V_{zz} \) results from the Hamiltonian \( \mathbf{H} + \lambda \mathbf{L} \mathbf{S} \), no further parameter is necessary.

Therefore in the \( \mathbf{4} \mathbf{T}_{2g} \) approximation with \( \mathbf{C}_{2v} \) symmetry seven parameters
\[ \delta, a, \theta, k, \alpha^2, H_L, H_S \]
determine the Mössbauer spectra in external magnetic fields.

3. Experimental results and interpretation. — Figure 1 shows the powder Mössbauer spectra at 4.2 K in longitudinal magnetic fields up to 50 kG. The isomer shift \( \delta_{\text{IS}} = 1.398 \pm 0.008 \ \text{mm/s} \) has been evaluated from least-squares analysis related to natural iron at 298 K.

The shift of ferrousfluosilicate has been measured once more. The obtained value \( \delta_{\text{IS}} = 1.411 \pm 0.008 \ \text{mm/s} \) slightly differs from 1.428 mm/s [6]. The measured difference of the isomer shifts of the two compounds is very small : 0.013 ± 0.008 mm/s.

The shape of the powder spectra in applied magnetic fields is typical for an almost axial ligand field symmetry which generates a susceptibility tensor \( \chi \) with \( \chi_L > \chi_0 \) at low temperatures [6]. Similar spectra were measured for ferrousfluosilicate. In this case a detailed analysis of susceptibility, proton resonance and Mössbauer data results in the plot of figure 2 [7] which shows the dependence of the hyperfine parameters \( H_L \) and \( H_S \) from \( \alpha^2 \) and \( k \) until | \( H_S \) | \( \leq | H_{\text{free Ian}} | \). Using
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**Fig. 2.** The parameter sets compatible with Mössbauer measurements of ferrousfluosilicate [7] are shown. The hyperfine constant $H_0 = 2 \mu_B < r_L^{-3}$ divided by $k$, the reduction factor of the spin-orbit coupling constant $\lambda = kl_{6e}$, and the covalency parameter $\alpha^2$ are plotted versus the Fermi contact field $H_c$. $k$ is assumed to be $k - 1$ and $k - \alpha^2$, given in brackets. $H_0/k$ is within less than 1 % independent of $k$. $H_c$ is limited by $\alpha^2 = 1$ and $|H_c| < |H_0^{\text{free ion}}| = 275$ kG. The values of these parameters are taken over for fitting the Mössbauer spectra of ferrousperchlorate (cf. text).

![Graph](image)

**Fig. 3.** The shape of the absorption lines on the left hand side at 50 kG calculated with $\theta = +6^\circ$ and $\alpha^2 - 0.94$ are shown for $k = 1$ and $k = \alpha^2$ (cf. text).

The intensities are not very well fitted. This is assumed to be caused by texture obvious from the

$H = 0$ kG quadrupole split spectrum, which shows different intensities for the two transitions.

Provided that the reduction of $\lambda$ is the same for $<r_L^{-3}>$, the quotient $H_0/k = 575$ kG = 4.7 a.u. represents an extrapolation to the free ion value. $H_0/k$ and $H_c$ agree very well with the theoretical free ion values [8] already mentioned in [7].

$\Delta E_0 = \Delta E_0/\alpha^2 F$, where the factor $F(\delta, a, \alpha^2, \lambda, T)$ reduces the quadrupole splitting by the spin-orbit coupling, is called the bar quadrupole splitting. The difference of $\Delta E_0$ in ferrousperchlorate (4.35 mm/s) and ferrousfluosilicate (4.60 mm/s) is 0.25 mm/s, a reasonable value to be related to the lattice contributions in both compounds.

The quadrupole moment $Q = \Delta E_0 / \left( \frac{2}{3} e^2 <r_L^{-3}> \right)$ becomes $Q = 0.19$ barn if $\Delta E_0$ is taken to be 4.6 mm/s and $<r_L^{-3}>$ is equated to $<r_L^{-3}> = 4.4 a_0^{-3}$.

4. Conclusion. — In this Mössbauer study of Fe(H$_2$O)$_6$(ClO$_4$)$_2$, results of the previous investigation of ferrousfluosilicate hexahydrate are involved. This concept is suggested because of the similar behaviour of the two Fe(H$_2$O)$_6$ molecules indicated by almost the same isomer shift at 4.2 K and nearly the same axial distortion of the ligand field. The advantage of this procedure is the possibility to fit all the seven parameters used in $T_{2g}$ approximation and $C_{2v}$ symmetry, the ligand field parameters $\delta, a, \theta$, the covalency parameter $\alpha$, the spin-orbit coupling constant $\lambda$, and the hyperfine constants $H_0, H_c$. The percolating spectra can only be understood by an eight per cent reduction of $\lambda$ relative to the free ion value. The total reduction of the spin-orbit coupling $\alpha S(l)$ then is $k\alpha^2 = \alpha^2 = 0.85$.

Susceptibility data are not available for the present. Single crystal measurements would proof the crystal field data and therefore the concept used.

It would be more reasonable to compare Fe(H$_2$O)$_6$ molecules dissolved in compounds of isomorphes series like M(H$_2$O)$_6$.SiF$_6$ with M = Mg, Co, Ni, Zn. The binding of Fe(H$_2$O)$_6$ to the environment is the same and the small differences of the ligand field para-
meter of one per cent relative to the cubic splitting will not be accompanied by a remarkable change of the molecular orbitals which determine the covalency, the spin-orbit coupling, and hyperfine constants. Such measurements are in progress.

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