

ON ELECTRIC FIELD GRADIENT AT Fe^{2+} IN $N_2H_5[Fe(N_2H_3COO)_3].H_2O$

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The crystal field split orbital states of ferrous ion in $N_2H_5[Fe(N_2H_3COO)_3].H_2O$ were calculated using perturbation theory. The ligands were assumed to be point charges with zero charge density in the vicinity of the ferrous ion, so the potential on its site could be expressed in terms of spherical harmonics⁽¹⁾:

$$U(r) = \sum_n^{\infty} \sum_{m=-n}^n A_{nm} r^m Y_{nm}(\theta, \varphi) \quad (1)$$

$$A_{nm} = \frac{4\pi}{2n+1} (-1)^n \sum_j e_j r_j^{n-1} Y_{nm}(\theta_j, \varphi_j) \quad (2)$$

The sum over j refers to the ions in the three chelate rings forming immediate environment of the metal ion. Spherical polar coordinates r_j, θ_j, φ_j , were defined in the orthogonal coordinate frame where y and z were parallel to the crystallographic b and c axis of isomorphous $N_2H_5[Ni(N_2H_3COO)_3].H_2O$ compound for which crystallographic data were known⁽²⁾. By operating with $U(r)$ on $3d$ electronic states $\gamma(r, \theta, \varphi) = R(r) Y_{2m}(\theta, \varphi)$ the following matrix elements were obtained:

$\sum_n \sum_{m=-n}^n A_{nm} \langle r^n \rangle \langle Y_{2m}(\theta, \varphi) | Y_{nm}(\theta, \varphi) | Y_{2m}(\theta, \varphi) \rangle$ which are nonvanishing for $n=0, 2$ and 4 . They were calculated using replacement theorem $Y_{nm} = c_{nj} T_{nm}$, with T_{nm} being the irreducible tensor defined by the angular momentum operators⁽¹⁾. First order perturbation theory yielded for the crystal field parameters $\Delta_1 = 1.6 \Delta_2$ and the corresponding electronic states $\varphi_i = \sum_j a_{ij} \gamma_j$. The electric field gradient tensor (EFG) arising from the valence electrons in these states was evaluated from: $\langle \varphi_i | V_{\alpha\beta} | \varphi_i \rangle = \sum_j \sum_k a_{ij}^* a_{ik} \langle \gamma_j | V_{\alpha\beta} | \gamma_k \rangle$ where $V_{\alpha\beta}$ represents the EFG operator⁽³⁾. For the estimated lowest level

$\varphi_0 = 0.7 |xy\rangle + 0.5 |yz\rangle - 0.4 |z^2\rangle + 0.3 |xz\rangle$ the major principal component of the EFG tensor (V_{zz}) could be either positive or negative. From further measurements of Mössbauer effect using single crystal of $N_2H_5[Fe(N_2H_3COO)_3].H_2O$ appropriate sign of V_{zz} and electronic ground state of ferrous ion will be determined.

References

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