The Mössbauer and magnetic resonances investigations of structural phase transitions in K$_2$ZnCl$_4$ crystals

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Abstract. The experimental data carried out by Mössbauer and magnetic resonances investigations of the structural phase transitions in K$_2$ZnCl$_4$ crystals are discussed by a simple electrostatic model, calculating, the lattice contributions to the local electric potential $V(r)$, electric field intensity $E(r)$ and electric field gradient tensor $V_{\alpha\beta}(r)$ and taking into account both the fractional electric point charges and rigid lattice approximations. The validity of the model is proved by a good fit of the computing results and experimental data of quadrupole splitting parameters at K sites obtained by $^{39}$K-NMR methods in high temperature incommensurate phase ($\sim$ Pnam symmetry). The experimental results obtained by Mössbauer and EPR methods in commensurate phase (Pna2$_1$ symmetry) of iron and copper doped K$_2$ZnCl$_4$ crystals are explained by relaxing the rigid lattice approximation. The insertion of probe ions appear to be done on not-exactly-Zn$^{2+}$ site.

PACS. 76.80.+y Mössbauer effect; other $\gamma$-ray spectroscopy

1 Introduction

Like many other members of the A$_2$BX$_4$ family [1], K$_2$ZnCl$_4$ shows the following sequence of structural phase transitions. There is at $T_i = 553$ K a transition from normal paraelectric phase with the space group Pnam ($b > a > c$) and four molecules per unit cell to an incommensurate phase ($q/a^* = (1 - \delta)/3$ with $\delta \ll 1$). At $T_c = 403$ K a lock-in transition to a commensurate ferroelectric phase ($q/a^* = 1/3$) with the space group Pna2$_1$ and 12 molecules per unit cell has evidenced. Also at $T_c = 145$ K there is another phase transition to a monoclinic commensurate ferroelectric phase with the space group A11a and 48 molecules per unit cell.

Very recently, a second low-temperature incommensurate phase between 152 K and 145 K has reported [2,3]. Quilichini [3] revealed by inelastic neutron scattering a soft optic phonon with a wave vector $q = 0.5b^* + (0.5 - \delta)c^*$, $\delta \ll 1$ responsible for this incommensurate phase transition. The structures and properties of some phases in K$_2$ZnCl$_4$ differ considerably from those of the prominent members of the A$_2$BX$_4$ family. The unusual feature is the presence, in the high temperature incommensurate phase, of large thermal hysteresis, memory effects and extremely slow relaxation of the dielectric constant [4].

In the present work the local electric potential, electric field intensity and static part of the lattice electric field gradient $(efg)$ behaviours at K sites in Pnam phase of K$_2$ZnCl$_4$ are probed by numerical calculations. These calculations have been performed using fractional ionic point charges and rigid lattice approximations respectively. We have extended the model relaxing the last approximation and allowing hopping of the sites along the $a$ axis and ferroelectric $c$ axis. We have evaluated the local electric properties dependencies with the displacement along one direction from the nominal cation sites. The computing results have compared with the experimental data obtained by NMR, Mössbauer and EPR methods on iron and copper doped potassium tetrachlorozincate.

2 Local electric properties computation

The lattice contribution to the local electric potential $V(r)$, intensity $E(r)$ and $V(r)$ tensor at cation sites $r_o(x_o, y_o, z_o)$ in the ferroelectric structure of K$_2$ZnCl$_4$ have been calculated by QSLATT3, a new version of the computing program QSCOMP [5]. The starting expressions are:

$$ V(r) = \frac{1}{4\pi\varepsilon_o} \int \frac{\rho(r')}{|r - r_o|} dr' $$

$$ E(r') = -\nabla V(r') $$

$$ efg = V_{\alpha\beta}(r) = -\nabla E(r) = \nabla(\nabla V(r)) = \begin{vmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{vmatrix} $$

where $\rho(r)$ is the lattice charge distribution around $r_o$ and $\varepsilon_o$ is the vacuum electric permittivity. The computing
procedure takes into account the point charge approximation of crystal field theory:

\[ \rho(\mathbf{r'}) = \sum_{i=1}^{N} q_i \delta(\mathbf{r'} - \mathbf{r}_i). \]  

In this approximation the lattice contributions to the local electric properties in \( \mathbf{r}_o \) are given by the relations:

\[
V_{\text{latt}}(\mathbf{r}_o) = \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^{N} \frac{q_i}{|\mathbf{r}_i - \mathbf{r}_o|},
\]

\[
E_{\text{latt}}(\mathbf{r}_o) = \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^{N} \frac{q_i (\mathbf{r}_i - \mathbf{r}_o)}{|\mathbf{r}_i - \mathbf{r}_o|^3},
\]

\[
V_{\alpha\beta}(\mathbf{r}_o) = \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^{N} \frac{q_i}{|\mathbf{r}_i - \mathbf{r}_o|^3} \left[ 3(x_{i\alpha} - x_{o\alpha})(x_{i\beta} - x_{o\beta}) - |\mathbf{r}_i - \mathbf{r}_o|^2 \delta_{\alpha\beta} \right].
\]  

The positions \( \mathbf{r}_i \) (and \( d_i = |\mathbf{r}_i - \mathbf{r}_o| \)) of the crystallographic cationic sites are given by the subroutine LATTICE according to the relation:

\[
\mathbf{r}_i = (x_{io} + la) \mathbf{i} + (y_{io} + mb) \mathbf{j} + (z_{io} + nc) \mathbf{k}
\]

where \( \mathbf{r}_o(x_{io}, y_{io}, z_{io}) \) designates the positions of the \( N_i^o \) charges \( q_i \) in the rectangular unit cell with the lattice constants \( a, b, c, (i = 1, 2, ..., N = (2l+1)(2m+1)(2n+1)N_i^o) \). The co-ordinates \( x_{io}, y_{io}, z_{io} \) and the lattice constants \( a, b, c \) for the studied structure are obtained from X-ray or neutron diffraction measurements. \( \delta \) is the Kronecker’s symbol. The values for charges \( q_i \) are given by the usual ionic charges or they can be obtained by other procedures, e.g. a valence summation, described recently in [7].

With the above mentioned quantities, the \( efg \) tensor components \( V_{\alpha\beta}(\mathbf{r}_i) \) are calculated by subroutine GRADIENT. The principal components \( V_{XX}, V_{YY}, V_{ZZ} \), and the asymmetry parameter \( (\eta = (V_{XX} - V_{YY})/V_{ZZ}) \), the corresponding eigen vectors and the Euler angles \( (\alpha, \beta, \gamma) \), between the \( efg \) tensor principal axes and the crystallographic axes, are obtained by the diagonalisation subroutine EIGEN.

The \( r^{-n} \) \( (n = 1, 2, 3) \) dependencies of local electric properties are more important for the ions directly coordinated to the central ion, i.e. for ligands, than more distant ions in the lattice.

On the other hand a complete neglect of distant ions may led to inaccuracies of the computing data and their comparison to the experimental ones. The new version of QSCOMP allows to calculate the local electric properties both of the ligand and also of the different surrounding shells contribution and the rest of lattice one.

\[
V_{\text{latt}}(\mathbf{r}_o) = V_{\text{lig}}(\mathbf{r}_o) + V_{\text{rest}}(\mathbf{r}_o)
\]

\[
E_{\text{latt}}(\mathbf{r}_o) = E_{\text{lig}}(\mathbf{r}_o) + E_{\text{rest}}(\mathbf{r}_o)
\]

\[
V_{\alpha\beta}(\mathbf{r}_o) = V_{\alpha\beta}^{\text{lig}}(\mathbf{r}_o) + V_{\alpha\beta}^{\text{rest}}(\mathbf{r}_o).
\]  

The dispersion of \( V, E \) and \( V_{\alpha\beta} \) values related to the shifted cationic position in the lattice is given by:

\[
V_{\text{latt}}(\mathbf{r}_o + \delta \mathbf{r}) = V_{\text{lig}}(\mathbf{r}_o) + \nabla V_{\text{rest}}(\mathbf{r}_o) \cdot \delta \mathbf{r}
\]

\[
E_\alpha(\mathbf{r}_o + \delta \mathbf{r}) = E_\alpha^{\text{lig}}(\mathbf{r}_o) + \nabla E_\alpha^{\text{rest}}(\mathbf{r}_o) \cdot \delta \mathbf{r}
\]

\[
V_{\alpha\beta}(\mathbf{r}_o + \delta \mathbf{r}) = V_{\alpha\beta}^{\text{lig}}(\mathbf{r}_o) + \nabla V_{\alpha\beta}^{\text{rest}}(\mathbf{r}_o) \cdot \delta \mathbf{r}.
\]  

3 Experimental

The electric quadrupolar hyperfine interaction between the probe and the neighbourhood can be evidenced by the NMR, NQR, Mössbauer and EPR experimental methods. The principal \( efg \) tensor components \( V_{\text{obs}} \) can be evaluated from the spectra by the relations

\[
V_{zz}^{\text{obs}} = \begin{cases} 
4.1357 \times 10^{-15} \frac{2\varepsilon_{obs}}{(1 - \gamma_{\infty})eQ_{\text{Fe}^{3+}}K} & \text{NMR, NQR method} \\
4.8038 \times 10^{-8} \frac{2\Delta E_{Q}^{\text{obs}}}{(1 - \gamma_{\infty})eQ_{\text{Fe}^{3+}}\sqrt{1 + \eta^2/3}} & \text{Mössbauer method} \\
1.1577 \times 10^{-8} \frac{P_{zz}^{\text{obs}}}{(1 - \gamma_{\infty})eQ_{\text{Cu}^{2+}}} & \text{EPR method}
\end{cases}
\]  

where \( \varepsilon_{obs}^{\text{Fe}}, \Delta E_{Q}^{\text{obs}}, P_{zz}^{\text{obs}} \) are the spectral parameters of the mentioned experimental methods. \( Q \) is the nuclear quadrupole moment and \( \gamma_{\infty} \) is the Sternheimer factor. The \( Q \) and values used in the calculus were \( Q^{(57\text{Fe})} = 0.21 \times 10^{-28} \text{m}^2, \gamma_{\infty}^{(57\text{Fe}^{3+})} = -10.6, Q^{(63\text{Cu})} = -0.15 \times 10^{-28} \text{m}^2, \gamma_{\infty}^{(63\text{Cu}^{2+})} = -25, Q^{(39\text{K})} = 0.09 \times 10^{-28} \text{m}^2 \) and \( \gamma_{\infty}^{(39\text{K})} = -20, [6,7] \). The numerical coefficients are energy conversion factors between the specific to eV units. The principals components of \( efg \) tensor, \( V_{\text{obs}} \) in \( \text{V/m}^2 \), given in Table 1, have extracted by a refined analyse of spectral parameters of hyperfine electric quadrupole interaction from the \( 39\text{K-NMR} \) spin-echo spectrum recorded in a superconducting magnet at Larmor frequency of \( \nu_L = 16.628 \text{MHz} \) [13], from \( 57\text{Fe}-\text{Mössbauer} \) spectra obtained in transmission geometry in the velocity range \( \pm 3 \text{ mm/s} \) using a \( 57\text{Co:Cu} \) source (50 mCi) with \( f = 0.73 \) and \( F_0 = 0.11 \text{ mm/s} \) [12] and from EPR spectra carried out with a JES ME-3X spectrometer with 100 kHz modulation [14], for pure and iron and copper doped \( K_2\text{ZnCl}_4 \) crystals. The temperature instability over the measuring period was less than 0.5 K.

The \( V_{\text{obs}} \) values are compared with the \( V_{\text{latt}} \) obtained from computing results taking into account the proposed model.

4 Computation results and discussions

4.1 Calculation of \( V_{\alpha\beta}(\mathbf{r}) \) on cation sites

The numerical computation of the lattice \( efg \) tensor at cation sites in \( K_2\text{ZnCl}_4 \) has been performed according to