Hyperfine study of Cu$_3$(ZrF$_7$)$_2$·16H$_2$O and its thermal decomposition

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By use of the time differential perturbed angular correlations technique, the hyperfine interactions at zirconium sites in Cu$_2$(ZrF$_7$)$_2$·16H$_2$O and its decomposition products were determined between 300 and 700 K. A simple model to give account of the decomposition process is presented in agreement with angular correlation and gravimetric results.

1. Introduction

Complex structures are known to be rather unstable at increasing temperatures and the possible chemical reactions, arising from this instability are an interesting field to study using both hyperfine and macroscopic techniques. As far as we know, no studies have been performed on the thermal behavior of Cu$_3$(ZrF$_7$)$_2$·16H$_2$O. The Cu$_3$(ZrF$_7$)$_2$·16H$_2$O compound crystallizes in the monoclinic P2$_1$/c space group (Z = 2) [1]. The crystal structure is formed by three different complex ions [Zr$_2$F$_{14}$]$^{6-}$, [Cu$_2$(H$_2$O)$_{10}$]$^{4+}$ and [Cu(H$_2$O)$_{6}$]$^{2+}$ linked by hydrogen bonds. The six copper atoms within the unit cell, are placed in two different surroundings in a 2 : 1 ratio. In the case of the anionic structure, the coordination polyhedra of each zirconium atom is a distorted Archimedean antiprism due to the Jahn–Teller effect originated by copper atoms [1].

In this paper the hyperfine interaction experienced by zirconium nuclei in Cu$_3$(ZrF$_7$)$_2$·16H$_2$O and its thermal decomposition products, is presented.

2. Experimental

The time differential perturbed angular correlations technique (TDPAC) allows to determine the hyperfine interaction between a radioactive nucleus, decay-

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ing through a two-step cascade, and its surrounding by measuring the time dependence of the angular distribution of the second emission relative to the direction of the first one.

For the case of quadrupole interactions, the perturbation arises from the electric field gradient (EFG) acting on the quadrupole moment \( Q \) of the intermediate nuclear level of the cascade. The interaction is described by the so called perturbation factor \( G_{22}(t) \) that can be written in the well known form [2]

\[
G_{22}(t) = \sigma_{20} + \sum_{n=1}^{3} \sigma_{2n} \cos(\omega_n t) e^{-\delta \omega_n t}.
\]

In eq. (1), \( \omega_n \) are already known functions of the quadrupole interaction frequency \( \omega_Q = e^2 Q V_{zz} / 4I(2I-1)\hbar \) and of the symmetry parameter \( \eta = (V_{xx} - V_{yy}) / V_{zz} \) of the EFG [2]; the \( \sigma_{2n} \) coefficients depend on \( \eta \) and \( \delta \) measures the \( \omega_Q \) distribution arising from defects and/or impurities of the lattice.

The effect of fluctuating EFGs can be described by use of the Abragam–Pound perturbation factor [3] deduced for fast relaxation processes, which can be written as

\[
G_{22}(t) = e^{-\lambda t},
\]

where \( \lambda \) is a function of the correlation time associated to the relaxation process.

Whenever the probes of a certain sample are occupying non-equivalent sites, the situation is described considering a linear superposition of perturbation factors \( G^i_{22}(t) \) as defined in eqs. (1) and/or (2),

\[
G_{22}(t) = \sum_i f_i G^i_{22}(t).
\]

The \( f_i \) coefficients are the relative fractions of each interaction.

A non-linear least-squares fitting program is used to derive the hyperfine quadrupole parameters \( \omega_Q \), \( \eta \) and \( \delta \) and the relative fractions \( f \) out of experimental data.

\( \text{Cu}_2(\text{ZrF}_7)_2.16\text{H}_2\text{O} \) hafnium doped samples were prepared by slow air evaporation of a solution of stoichiometric amounts of \( \text{ZrF}_4 \) and \( \text{CuF}_2 \) in water following the method outlined by Marignac [4]. The samples were checked using X-ray powder diffraction analysis in order to ensure that the compound was properly prepared.

The \( 133-482 \text{ keV} \gamma-\gamma \) cascade of \( ^{181}\text{Ta} \) used in this work as TDPAC probe was obtained by thermal neutron irradiation of the \( ^{180}\text{Hf} \) impurities. Measurements were performed using a two-CsF-detector high-resolution setup (\( 2\tau = 0.75 \text{ ns at Ta energies} \)). An electric furnace permitted to heat the samples, in situ. The temperature of the samples was stable within \( \pm 1 \text{ K} \).