Hyperfine study of $Cu_3(ZrF_7)_2 \cdot 16H_2O$ 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 $Cu_2(ZrF_7)_2 \cdot 16H_2O$ 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 $Cu_3(ZrF_7)_2 \cdot 16H_2O$. The $Cu_3(ZrF_7)_2 \cdot 16H_2O$ compound crystallizes in the monoclinic $P2_1/c$ space group ($Z = 2$) [1]. The crystal structure is formed by three different complex ions $[Zr_2F_{14}]^{6-}$, $[Cu_2(H_2O)_{10}]^{4+}$ and $[Cu(H_2O)_6]^{2+}$ 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 $Cu_3(ZrF_7)_2 \cdot 16H_2O$ 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]

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

In eq. (1), ω_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 σ_{2n} coefficients depend on η and δ measures the ω_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

$$G_{22}(t) = e^{-\lambda t} , \tag{2}$$

where λ 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 $G_{22}^{i}(t)$ as defined in eqs. (1) and/or (2),

$$G_{22}(t) = \sum_{i} f_i G_{22}^{i}(t) . \tag{3}$$

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 ω_Q, η and δ and the relative fractions f out of experimental data.

$Cu_2(ZrF_7)_2 \cdot 16H_2O$ hafnium doped samples were prepared by slow air evaporation of a solution of stoichiometric amounts of ZrF_4 and 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 keV γ–γ cascade of [181]Ta used in this work as TDPAC probe was obtained by thermal neutron irradiation of the [180]Hf impurities. Measurements were performed using a two-CsF-detector high-resolution setup ($2\tau = 0.75$ ns at Ta energies). An electric furnace permitted to heat the samples, in situ. The temperature of the samples was stable within ± 1 K.

3. Results and discussion

The study of Cu$_2$(ZrF$_7$)$_2$·16H$_2$O was performed between 296 and 705 K. Results showing the hyperfine parameters obtained by fitting are displayed in table 1 and fig. 1. At room temperature the TDPAC spectrum (fig. 2) was fitted assuming a single quadrupole interaction acting on the probes. This one-interaction picture is in agreement with the crystallographic structure reported in ref. [1]. In addition, point charge calculations of the electric field gradient at zirconium sites yield an asymmetry parameter ($\eta_{calc} = 0.79$) in good agreement with the experimental one ($\eta_{exp} = 0.72_2$).

On heating, the interaction observed at room temperature was replaced by another having two components: a static interaction and a dynamic one, 60 and 40% populated at 352 K, respectively (see table 1). Between 352 and 414 K the relative fraction of the static interaction increased at the expense of the relative fraction of the dynamical one. Within this temperature range the quadrupole frequency of the static interaction rises and, from 414 K on it remains nearly constant. It should be noticed that at 414 K the dynamical interaction disappeared.

In the range from 520 to 557 K the static interaction just mentioned vanished in two steps. It was observed that at 520 and 543 K the quadrupole parameters of the new interaction were different from those determined at 549 and 557 K (see table 1 and open circles and open triangles in fig. 1). From 586 to 700 K a new single hyperfine interaction was fitted to the spectra (asterisks in fig. 1).

In order to understand the meaning of the changes observed in the hyperfine parameters, a differential thermogravimetric analysis (DTG) was performed at a rate of 5 K/min at atmospheric pressure between 296 and 1000 K. Sharp mass losses at 346, 412 and 557 K (clearly owing to low activation energy processes) and two broad superimposed signals (already seen in oxidation processes [5,6]) were determined (see fig. 3). The start and peak temperatures of the thermogravimetric signals were indicated as dotted and solid vertical lines in fig. 1a respectively. From this figure it is apparent that the changes observed with both techniques have the same origin.

Table 1
Hyperfine parameters obtained from TDPAC spectra at selected temperatures.

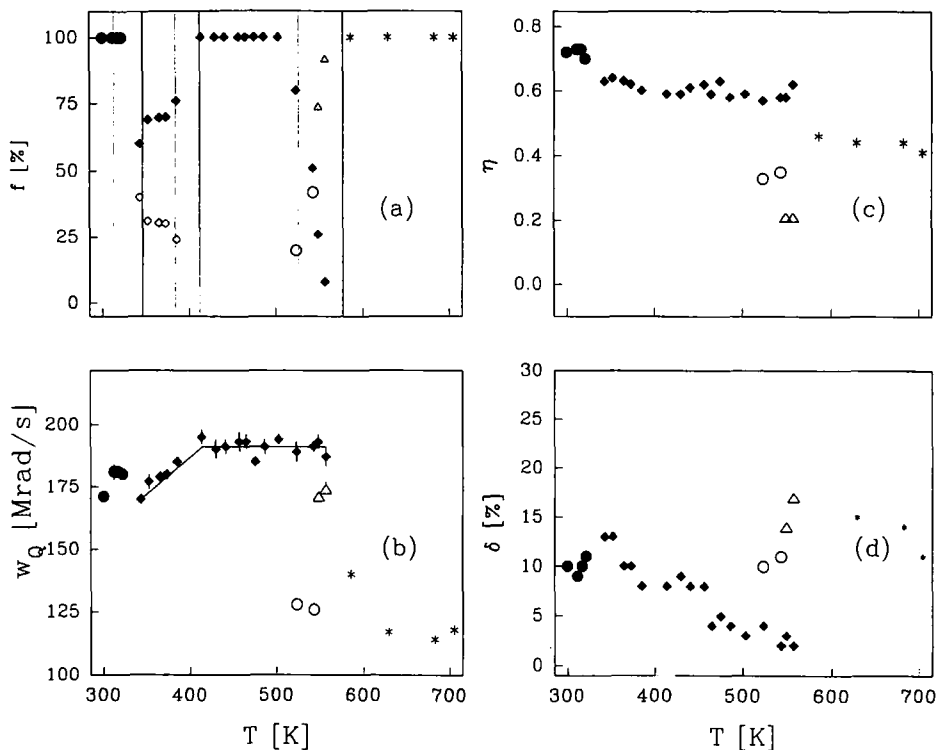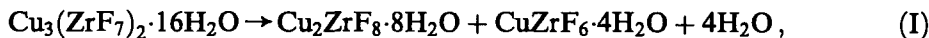| T (K)	f (%)	ω_Q (Mrad/s)	η	δ (%)
296	100	171$_2$	0.72$_2$	11$_2$
352	60$_3$	177$_2$	0.64$_3$	13$_2$
352	40$_2$		$\lambda = 36_{10}$ Mrad/s	
523	76$_3$	189$_4$	0.57$_3$	2$_1$
523	24$_2$	126$_4$	0.35$_3$	11$_3$
549	26$_4$	193$_5$	0.58$_4$	3$_2$
549	74$_5$	171$_7$	0.21$_4$	14$_5$

Fig. 1. Relative fractions (a), quadrupole interaction frequencies (b), asymmetry parameters (c) and distribution widths (d) obtained from TDPAC data in the whole thermal range.

According to DTG data we can conclude that a mechanism to give account of the analysis can be established as follows:

$$Cu_3(ZrF_7)_2 \cdot 16H_2O \rightarrow Cu_2ZrF_8 \cdot 8H_2O + CuZrF_6 \cdot 4H_2O + 4H_2O \,, \tag{I}$$

$$Cu_2ZrF_8 \cdot 8H_2O \rightarrow CuZrF_6 \cdot 4H_2O + CuF_2 + 4H_2O \,, \tag{II}$$

$$CuZrF_6 \cdot 4H_2O \rightarrow CuZrF_6 + 4H_2O \,, \tag{III}$$

where each of the reactions can be associated to one of the sharp signals in the DTG. The existence of $Cu_2ZrF_8 \cdot 8H_2O$ at temperatures higher than room temperature is a reasonable assumption taking into account that, as it was reported in ref. [7], four of the twelve water molecules in $Cu_2ZrF_8 \cdot 12H_2O$ have bond distances at least 20% larger than the mean bond distance.

Based on this scheme it is possible to interpret the evolution of the hyperfine interactions observed as follows: the change of the one-site interaction to the two-site one (at 350 K) is due to the reaction proposed in eq. (I). The peculiar behavior of the relative fractions in the 350–414 K range (see fig. 1a) is clearly supported
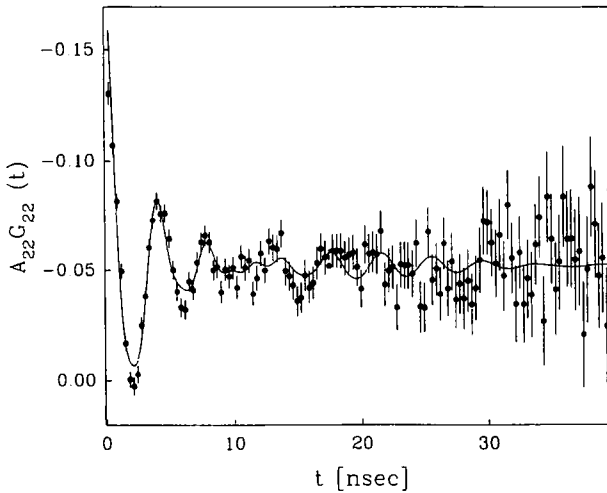
Fig. 2. TDPAC spectrum obtained at room temperature. Solid line is the fit using the parameters of the first row in table 1.

by the reaction presented in eq. (II) that indicates that as the $Cu_2ZrF_8 \cdot 8H_2O$ is produced it decomposes to $CuZrF_6 \cdot 4H_2O$. So the static interaction is related to $CuZrF_6 \cdot 4H_2O$ and the dynamical one to $Cu_2ZrF_8 \cdot 8H_2O$. Additional support to the former assignment is obtained from point charge calculations of the asymmetry parameter of the EFG of $CuZrF_6 \cdot 4H_2O$. The value obtained $\eta_{calc} = 0.65$ is in good agreement with the experimental result.

It is clear that the last sharp signal of the DTG indicates the dehydration of the $CuZrF_6 \cdot 4H_2O$ compound (eq. (III)). So, the new interaction determined at 520 K (represented by open circles in fig. 1) corresponds to $CuZrF_6$.

As it can be seen in fig. 3, the last sharp peak is overlapped with broad signals already reported to exist during oxidation processes. Then, it is likely to expect a short range of stability of $CuZrF_6$ and its replacement by oxidation products. So, the hyperfine interactions determined at 549 and 557 K (open triangles in fig. 1) and from 586 K on (asterisks in fig. 1) could be interpreted as the interactions related to oxidation products. The oxidation process is not clearly understood yet. The fact that the last hyperfine interaction observed (asterisks) approaches the well known interaction of the monoclinic ZrO_2 [8], strongly suggests that the evolution of the interactions represents the oxidation stages.

4. Conclusions

TDPAC results together with DTG studies allowed to determine the following thermal behavior of $Cu_3(ZrF_7)_2 \cdot 16H_2O$.

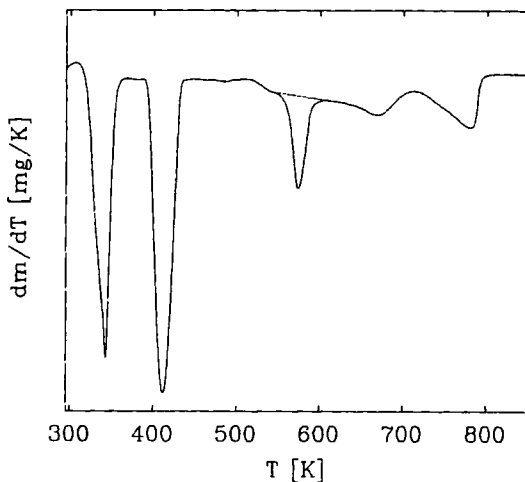Fig. 3. Differential thermogravimetric analysis (schematic) obtained from $Cu_3(ZrF_7)_2 \cdot 16H_2O$ samples.

– Above room temperature, the $Cu_3(ZrF_7)_2 \cdot 16H_2O$ compound is stable along a narrow range ($\sim 50\,K$).

– The reaction path proposed in eqs. (I)–(III) is in good agreement with both TDPAC and DTG results and the hyperfine interactions of $Cu_2ZrF_8 \cdot 8H_2O$, $CuZrF_6 \cdot 4H_2O$ and $CuZrF_6$ are inferred.

References

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