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PAC study of martensitic transformations in RCu compounds

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Abstract

The martensitic transformation from the cubic CsCl-type to the orthorhombic FeB-type structure of RCu (R = Gd, Tb and Y) compounds has been investigated by perturbed angular correlation (PAC) measurements of the nuclear electric quadrupole interaction (QI) at ^{111}Cd probe nuclei on the Cu site as a function of temperature. The QI data indicate that the martensitic transition extends over a finite temperature range and affects only part of the samples. The transition ranges are $190\,K < T < 250\,K$, $80\,K < T < 150\,K$ and $60\,K < T < 120\,K$ for GdCu, YCu and TbCu, respectively, with saturation values between 40 and 60 percent. The temperature dependence of the QI parameters in the FeB-type structure is independent of the R constituent. The order of magnitude of the magnetic hyperfine interaction in the FeB-type structure has been estimated from the low temperature PAC spectra.

PACS: ■; ■; ■

Keywords: Martensitic transformations; Nuclear quadruple interaction; Magnetic hyperfine field; PAC spectroscopy; Rare earth magnetism

1. Introduction

The structure of the equiatomic rare earth (R) compounds RCu changes with the atomic number of the rare earth constituent. RCu with light R constituents crystallize in the orthorhombic FeB-type structure, those with heavy R constituents in the CsCl-type structure ($Pm\bar{3}m$). The compounds with R = Gd, Tb and Y present a lattice instability. In these cases the system may undergo a martensitic transformation (MT) from the cubic CsCl structure to the orthorhombic FeB-type structure at 250, 117 and 140 K, respectively [1]. This transformation has been extensively studied by measurements of electrical resistivity, magnetic susceptibility and thermal expansion [2–7]. X-ray absorption spectroscopy has provided evidence for a modification of the electronic structure, which suggest that the s–d hybridization plays a major role for the transformation.

While YCu is a Pauli paramagnet, GdCu and TbCu show spontaneous antiferromagnetic order [8,9]. The Neel temperatures are $T_N^{CsCl} = 150$ and 117 K and $T_N^{FeB} = 45$ K and 48 × K for the CsCl-type and the FeB-type structures of GdCu and TbCu, respectively.

In the present contribution, we report an investigation of the MT of RCu, R = Gd, Tb, Y by measurements of the electric quadrupole interactions (QI) of a nuclear quadrupole moment Q with the electric field gradient (EFG) acting at the nuclear site. These measurements were carried out with the perturbed angular correlation (PAC) technique using the isotope ^{111}Cd as probe nucleus.

QI is usually expressed by two parameters, the quadrupole frequency $\upsilon_q = eQV_{zz}/h$ and the asymmetry parameter $\eta = V_{xx} - V_{yy}/V_{zz}$ where $V_{ii} = \delta^2 V/\delta_i^2$ $(i = x, y, z)$ are the principal axes components of the diagonalized EFG tensor. QI measurements may distinguish between the CsCl- and the FeB-type structures of RCu: Whereas a finite, axially asymmetric EFG is expected for both sites of orthorhom-

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bic FeB, the EFG and thus the QI vanishes on both sites of the cubic CsCl-type structure.

2. Experimental details

The PAC measurements were carried out with the 171–245 keV cascade of ^{111}Cd, which is populated by the electron capture decay of the 2.8 d isotope ^{111}In. A standard 4-detector BaF_2 setup was used, equipped with a closed-cycle He refrigerator for temperature variation in the range $8\,K \leqslant T \leqslant 300\,K$. Details on the PAC technique can be found in Refs.[10,11]. Samples of RCu, R = Gd, Tb, Y were produced by arc melting of the metallic components in the stoichiometric ratio in an argon atmosphere. To improve homogeneity, the buttons were melted several times. One part of these samples was doped with the PAC probe ^{111}In/^{111}Cd by diffusion, under Ar atmosphere (800 °C, 12 h), of carrier-free ^{111}In into the host lattices. The other part was used for X-ray diffraction (XRD) characterization. All samples were found to have the $Pm\bar{3}m$ cubic crystal structure. In the case of TbCu, a very weak contamination by $TbCu_7$ was detected.

3. Results and discussion

For the analysis of the PAC spectra of RCu, R = Gd, Tb and Y, it is important to know the site preference of the probe nucleus. For an answer to this question, we have first carried out a measurement of ^{111}Cd in DyCu.

DyCu exists only in the cubic CsCl structure with antiferromagnetic order below $T_N = 64\,K$ [12,13]. Fig. 1 shows the PAC spectra of ^{111}Cd in this compound at 300 and 8 K. At both temperatures one finds a constant anisotropy, nonmodulated in time. This implies the absence of any perturbing hyperfine interaction in both the paramagnetic and the antiferromagnetic phase. Because of the cubic symmetry a vanishing EFG is expected for both the Dy and the Cu site. The absence of magnetic hyperfine interaction in the antiferromagnetic phase, however, leads to the conclusion that ^{111}Cd resides on the Cu site. Only for this site all hyperfine field contributions of the antiferromagnetic structure cancel. For ^{111}Cd on the R site a finite magnetic hyperfine field is expected.

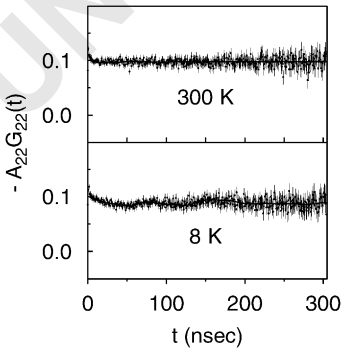

Fig. 1. PAC spectra of ^{111}Cd in DyCu at 300 and 8 K.

Figs. 2 and 3 show typical PAC spectra of ^{111}Cd in YCu and GdCu measured at different temperatures. Starting at 300 K, the compounds were cooled in several steps to 8 K and subsequently heated back to room temperature (RT). In all compounds, the RT PAC spectra show a constant, unperturbed anisotropy which implies a vanishing QI and thus confirms that the RCu compounds are cast in the cubic CsCl-type structure. Towards lower temperatures, a nonperiodic modulation of the anisotropy appears in the compounds RCu with R = Gd, Tb, Y. Although GdCu and TbCu show spontaneous magnetic order below

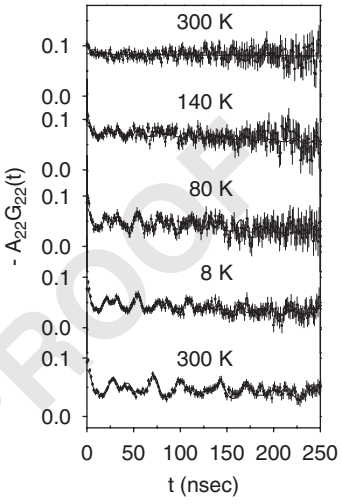

Fig. 2. PAC spectra of ^{111}Cd in YCu at different temperatures. The compound was cooled from room temperature (RT) (topmost spectrum) to 8 K and subsequently heated back to RT (bottommost spectrum).

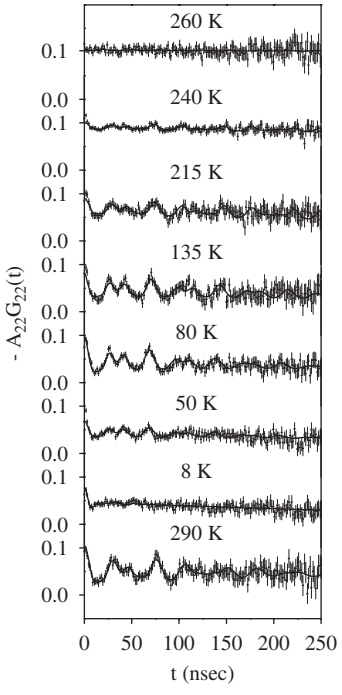

Fig. 3. PAC spectra of ^{111}Cd in GdCu at different temperatures. The compound was cooled from room temperature (RT) (topmost spectrum) to 8 K and subsequently heated back to RT (bottommost spectrum).

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$T_N^{CsCl} = 150$ and 117 K, respectively, the ^{111}Cd:DyCu spectra indicate that a perturbation by magnetic hyperfine interaction can be excluded as long as the compounds are in the CsCl-type structure.

The nonperiodicity of the modulation, the amplitude of which increases with decreasing temperature, reflects a perturbation by an axially asymmetric EFG and this component can therefore be attributed to ^{111}Cd probe nuclei in the orthorhombic FeB-type structure of RCu. After the martensitic transition the FeB-type structure is stable at $T \leqslant 300$ K, as can be seen in Figs. 2 and 3.

Based on the above considerations, the spectra at $T_N^{FeB} \leqslant T < 300$ K were analyzed by fitting the expression

$$G_{kk}(t) = f_{FeB} G_{kk}^{FeB}(t) + f_{CsCl} G_{kk}^{CsCl}(t) \quad (1)$$

to the measured data. $G_{kk}^{FeB}(t)$ and $G_{kk}^{CsCl}(t)$ are the theoretical perturbation factors for an axially asymmetric QI and a vanishing hyperfine interaction, respectively. $G_{kk}^{FeB}(t)$ is a function of the quadrupole frequency υ_q and the asymmetry parameter η, $G_{kk}^{CsCl}(t) = 1$ [10]. f_{FeB} and f_{CsCl} are the relative intensities of the two structures, with $f_{FeB} + f_{CsCl} = 1$. The results of the analysis for YCu and GdCu, expressed by the parameters f_{FeB}, υ_q and η are collected in Fig. 4. In agreement with the neutron diffraction results of Blanco et al. [8] for GdCu we find that the martensitic transition affects only part of the samples and extends over a finite temperature range. For GdCu our data indicate a transition range of 190 K $< \cap$ $T < 250$ K, for YCu the range is 80 K $< T <$ 150 K with saturation values $f_{FeB}(8\,K) \sim 0.6$ and 0.4, respectively.

In the case of TbCu, the FeB component appeared at $T \sim 120$ K, which agrees with the temperature of the martensitic transition reported by other authors. The fraction f_{FeB} increased with decreasing temperature, saturating at $f_{FeB} \sim 0.15$ in the first cooling cycle. With such a small percentage of the FeB-type structure, a precise determination of the QI parameters is difficult. In an attempt to raise the fraction f_{FeB}, the sample of TbCu was repeatedly cycled between 300 and 77 K. As shown in Fig. 5, with about 5 cycles the percentage of the FeB-type could be increased to almost 50. The thermal cycling probably releases stresses which are known to stabilize the CsCl-type structure [8]. The QI parameters ν_q and η measured with this sample are shown in Fig. 3 as a function of increasing temperature.

The temperature dependence of the quadrupole parameters is practically the same in all the three compounds investigated. From a constant value below 77 K, the quadrupole frequencies decrease by about 10 percent between 77 and 300 K. While the absolute value of the frequencies varies slightly with the R constituent, the asymmetry parameter is within the errors same for all three compounds.

Comparing the low-temperature spectra in Figs. 1 and 2, one notes that while in paramagnetic YCu the FeB modulation persists down to 8 K, in the spectra of GdCu its amplitude starts to decrease at $T \sim T_N^{FeB} = 45$ K, and at $T = 8$ K the modulation has completely disappeared. This difference reflects the different magnetic properties of YCu and GdCu. In FeB-type GdCu spontaneous helimagnetic order [8] sets in at $T_N^{FeB} = 45$ K, giving rise to a finite magnetic hyperfine field B_{hf} at the probe nucleus. The angular correlation is then perturbed by a combined magnetic and electric hyperfine interaction and in addition to the QI parameters ν_q and η, the PAC spectra depend on the magnetic interaction frequency $\nu_M = g\mu_N B_{hf}/h$ (g denotes the nuclear g factor) and the Euler angles $ß$, γ which describe the orientation of B_{hf} relative to the principal axes of the EFG tensor [14]. The low-temperature GdCu spectra suggest that the magnetic and the electric interactions are of comparable strength because in this case the oscillatory structure of the spectra tends to be strongly damped. We have estimated the order of magnitude of the magnetic hyperfine field by fitting the parameters ν_M and $ß$

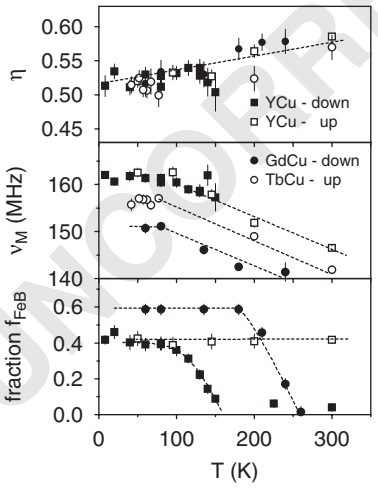

Fig. 4. The quadrupole frequency and the asymmetry parameter of ^{111}Cd in the FeB-type structure of YCu (full and open squares, respectively), GdCu (full points) and TbCu (open points) as a function of temperature. The bottommost section shows the evolution of the FeB-type fraction upon cooling from 300 K. The full squares stand for the cooling sequence of YCu to 8 K; the open squares illustrate the subsequent heating to room temperature. The full points correspond to the cooling sequence of GdCu.

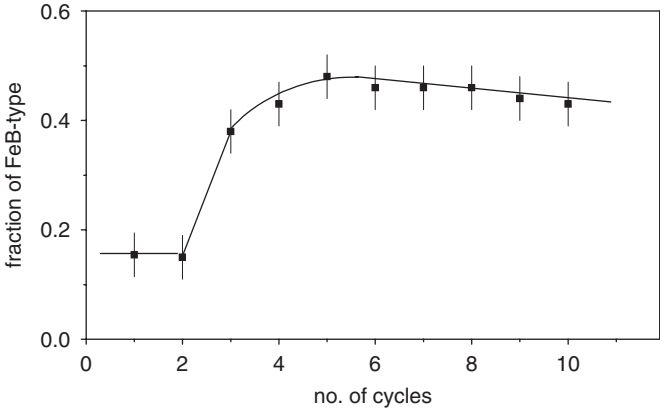

Fig. 5. The growth of the FeB-type structure of TbCu at room temperature induced by cycling the compound between 300 and 77 K.

of the theoretical perturbation factor for a combined interaction [14] to the 8 K spectrum of GdCu. Fixing ν_q and η to the values observed at 60 K and assuming $\gamma = 0$, the 8 K spectrum can be rather well reproduced with a magnetic hyperfine field $B_{hf} \sim 3$ T and an angle $ß = 0^\circ$. If $ß$ is fixed to 90°, one obtains $B_{hf} \sim 6$ T. At smaller fields, the quadrupole oscillations would become visible, at larger fields a magnetic oscillation pattern would appear.

The low-temperature spectra of TbCu after thermal cycling resemble those of GdCu. Here too, the attenuation of the FeB component sets in at $T \sim T_N^{FeB} = 48$ K and the magnetic hyperfine field needed to explain the 8 K spectrum is of the same order of magnitude as in GdCu.

4. Summary

It has been shown that measurements of electric quadrupole interactions are a useful tool for the investigation of structural phase transitions. In this report, the perturbed angular correlation technique with ^{111}Cd as probe has been used to look at the martensitic transformations of the compounds RCu, R = Gd, Tb, and Y. The transitions were found to be irreversible and gradual in character, extending over a temperature range of about 60 K. At most, 60 percent of each sample transformed to the FeB-type structure. The temperature dependence of the QI parameters of ^{111}Cd in the FeB-type structure has been determined and the order of magnitude of the magnetic hyperfine field in the helimagnetic phases has been estimated.

Acknowledgments

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