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Polymorphic Phase Transformation in In_2La and $CeIn_2$

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Abstract. Nuclear quadrupole interactions of ^{111}Cd probes in In_2La and $CeIn_2$ were measured using perturbed angular correlation of gamma rays (PAC). Near room temperature, a single non-axially symmetric quadrupole interaction was observed in each compound, with $\omega_0 = eQV_{zz}/\hbar$ = 78.8(2) Mrad/s and η = 0.312(1) for In_2La at 11 °C and ω_0 = 80(1) Mrad/s and η = 0.29(2) for $CeIn_2$ at 34 °C. The observed non-axial symmetry is consistent with the reported $CeCu_2$ structure of the phases. The non-axially symmetric interactions were replaced completely by axially symmetric interactions (η = 0) at 524 °C, with ω_0 = 101.0(1) Mrad/s in In_2La and ω_0 = 96.9(4) Mrad/s in $CeIn_2$. The change in symmetry is attributed to a polymorphic phase transformation. Based on symmetry information from the quadrupole interaction and on chemical arguments, it is proposed that high-temperature phases of In_2La and $CeIn_2$ both have the AlB_2 (C32) structure.

Key Words: PAC, phase transformation, polymorph, quadrupole interaction.

1. Introduction

In_2La and $CeIn_2$ compounds have the $CeCu_2$ structure at room temperature [1] and reportedly maintain this structure up to their melting points [2]. Using the method of perturbed angular correlation of gamma rays (PAC), the quadrupole interaction at nuclei of ^{111}Cd probes on the In sublattice has been measured in each compound. Quadrupole interactions measured near room temperature were found to be non-axially symmetric, as expected for the reported $CeCu_2$ structure. However, quadrupole interactions measured at 524 °C were found to be axially symmetric in both compounds and, moreover, to have very similar parameters. This is taken to indicate the existence of a polymorphic phase transformation in both systems to a previously unknown high temperature structure of $CeIn_2$ and In_2La.

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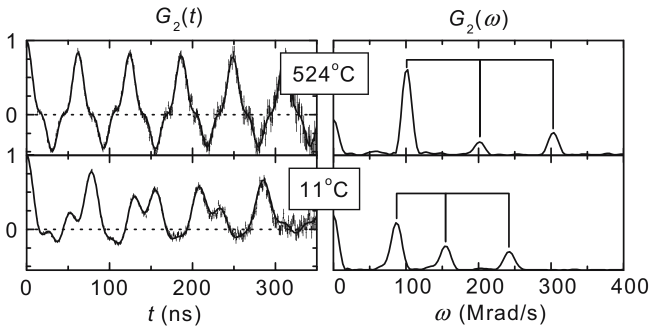

Figure 1. PAC spectra and Fourier transforms of ^{111}Cd in In_2La at indicated temperatures.

A previous report of measurements on In_2La and experimental methods can be found in [3]. Representative PAC spectra of In_2La from that work are shown in Figure 1 for measurements at 11 °C (bottom) and at 524 °C (top). A single quadrupole interaction is observed at 11 °C with $\omega_0 = eQV_{zz}/\hbar = 78.8(2)$ Mrad/s and $\eta = 0.312(1)$, in which ω_0 is the quadrupole interaction frequency and η is the asymmetry parameter of the electric field gradient tensor. At 524 °C, this signal is completely replaced by an axially symmetric signal with $\omega_0 = 101.0(1)$ Mrad/s. At intermediate temperatures, both signals were observed, and site fractions exhibited hysteresis between 200 and 450 °C characteristic of a first order phase transformation. Changes in the quadrupole interactions were reversible when cycling up and down in temperature. More detailed information about site fractions and temperature dependencies of hyperfine parameters can be found in [3].

2. Experiment

For the present work, a Ce–In sample was prepared having a composition of $28.0^{+0.9}_{-1.8}$ at.% Ce, which is in the two-phase field of the Ce–In phase diagram between $CeIn_2$ and $CeIn_3$. Representative spectra are shown in Figure 2 for measurements at 34 °C (bottom) and at 524 °C (top). Two quadrupole interaction signals were observed at 34 °C. One signal had a site fraction of 0.73(4) with $\omega_0 = 73.4(1)$ Mrad/s and was axially symmetric ($\eta = 0$), which is in excellent agreement with the signal previously observed for ^{111}Cd in $CeIn_3$ [4]. The second signal had quadrupole interaction parameters $\omega_0 = 80(1)$ Mrad/s and $\eta = 0.29(2)$, and is attributed to ^{111}Cd on the In site in $CeIn_2$. It can be seen that these latter values are very similar to those observed for In_2La near room temperature cited above. At 524 °C, the signal for $CeIn_3$ is still present, with a frequency slightly lower than that observed near room temperature, which is attributed to thermal expansion, while the signal for $CeIn_2$ is completely replaced by an axially

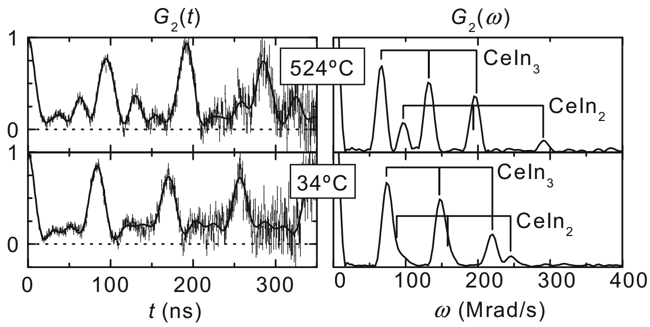

Figure 2. PAC spectra and Fourier transforms at indicated temperatures of ^{111}Cd in a sample containing a mixture of $CeIn_2$ and $CeIn_3$ phases.

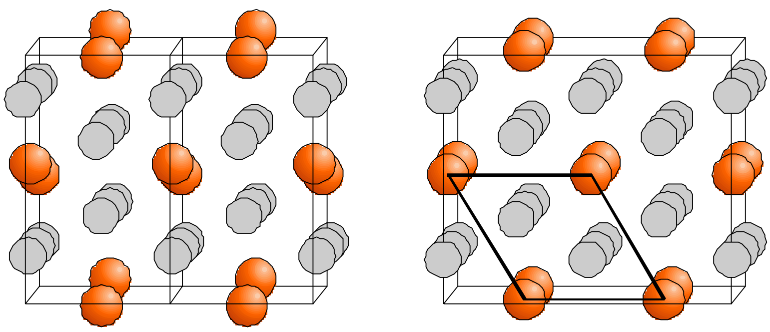

Figure 3. Crystal structures of $CeCu_2$ (*left*) and AlB_2 (*right*), with Ce and Al atoms shown in *light grey* and Cu and B in *dark grey*. On the left, some atoms lying outside the unit cells have been drawn to make comparison easier (adapted from [5]).

symmetric signal having ω_0 = 96.9(4) Mrad/s. All signals exhibited negligible inhomogeneous broadening.

3. Discussion and conclusions

Observation of an axially symmetric quadrupole interaction at elevated temperature can only come from probes in a structure that differs from $CeCu_2$. In principle, point defects formed at elevated temperature might disturb quadrupole interactions at probe nuclei in the $CeCu_2$ structure, leading to new signals. In such a case, one would observe one or more of the following: inhomogeneous broadening, multiple signals due to different local arrangements of defects, and signals with $\eta > 0$. The PAC signals observed at high temperature are inconsistent with any of these characteristics, and therefore are attributed to probes in a new polymorph with symmetry higher than in the $CeCu_2$ structure. More specifically, observation of $\eta = 0$ requires that there be a single 3-, 4- or 6-fold axis of symmetry at the lattice location of the probe. Because quadrupole interactions of ^{111}Cd probes are observed immediately after decay of parent ^{111}In activity, the probes are located at In lattice locations.

A survey of all common MX_2 compounds (M = metal; X = group IB, IIB, IIIB, IVB elements) listed in Pearson's handbook [1] showed that only four structures have symmetries at the X site that give $\eta = 0$: AlB_2, Cd_2Cd, $CaIn_2$ and $MoSi_2$ [3]. Of these four structures only the AlB_2 structure has been observed for MX_2 compounds in which M and X are both trivalent elements. Therefore, the high-temperature polymorph is believed to have the AlB_2 structure [3]. The $CeCu_2$ and AlB_2 crystal structures are compared in Figure 3. As can be seen, the $CeCu_2$ structure (left) arises through slight distortions of the hexagonal AlB_2 structure (right) that destroy the 3-fold rotational symmetry around the B-site.

The very close values of quadrupole interaction parameters in $CeIn_2$ and In_2La in both LT and HT phases suggest that the phase transformations are of the same type in both systems. Attempts to determine the structure of the high temperature phase of In_2La by X-ray powder diffraction failed due to extremely rapid out-diffusion and oxidation of La [3]. No similar attempt was made for $CeIn_2$ because the same result was expected. However, PAC measurements were readily carried out over weeks using samples in ingot form under vacuum in a pressure less than 5 μPa.

Acknowledgements

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