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The Stability of Icosahedral Cd-Yb

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ABSTRACT

The stability of single-crystalline icosahedral Cd-Yb was investigated using X-ray diffraction methods in the temperature range 20 K \( \leq T \leq 900 \) K at ambient pressure and from ambient temperature to 873 K at about 9 GPa. Single-crystals remain stable at low temperatures and in the investigated HP-HT-regime. At high temperatures and ambient pressure, the quasicrystal decomposes. The application of mechanical stress at low temperatures yields to the same decomposition, the formation of Cd. A reaction of icosahedral Cd-Yb with traces of oxygen or water causing the decomposition seems reasonable, but a low-temperature instability of this binary quasicrystal cannot be ruled out totally.

INTRODUCTION

What stabilizes quasicrystals? Are they stabilized by energy or entropy? Energy stabilization would mean that the quasicrystalline state is a ground state of matter. In case of entropy stabilization, quasicrystals would only be stable in a high temperature regime. The recently discovered congruently melting binary icosahedral Cd_{5.7}Yb [1] could be very valuable to answer this question. As icosahedral Cd_{5.7}Yb and its neighboring approximant phases Cd_{6}Yb and Cd_{3.6}Yb are line phases [2], chemical disorder can be excluded as essential entropic contribution. Therefore, the stability of icosahedral Cd_{5.7}Yb at non-ambient conditions can give valuable hints to answer the question of stabilization. The corresponding icosahedral Cd-Ca was found to be stable at ambient conditions [3]. At 110 K, an order-disorder transition was reported for the cubic Cd_{6}Yb approximant [4], which is also visible as anomalies in electrical resistivity and thermal conductivity, but was not found for the icosahedral Cd-Yb [5]. At high pressures, icosahedral Cd-Yb seems to remain stable up to 40 GPa [6].

EXPERIMENTAL DETAILS

Icosahedral Cd-Yb was synthesized from appropriate quantities of Cd and Yb (4N) in a sealed Ta-crucible with a low partial pressure of ultrahigh purity Ar. The alloy was homogenized three times at 670 °C for one hour with a 180 ° rotation of the crucible between each step. Single crystals were grown by the use of the Bridgman technique. The homogenized alloy was heated to 800 °C and after one hour the crystal was grown with a pulling speed of 1 mm/hr. A single-crystalline sample was oriented and sectioned from the ingot. After dividing it into smaller grains, selected single crystals were stored in a glove-box under Argon atmosphere. X-ray diffraction experiments were carried out on a mar300 image-plate system with Mo-Kα radiation (Johansson monochromator, RAG 50 kV, 80 mA). For Laue experiments the monochromator
was removed. Powder diffraction experiments were done on a Stoe Stadi-P powder diffractometer using Cu-Kα radiation. A Retsch MM-2 mixer mill was used for (high-energy) ball milling of the samples. Typically ca. 8 mm$^3$ of single crystalline icosahedral Cd-Yb and a steel ball (12 mm diameter) were put into a gas-tight steel grinding jar (volume 1.5 cm$^3$) inside the glove-box. For milling, the jar was cooled by liquid nitrogen. After milling, the opening of the jar and all further handling of the sample was done in the glove-box. High-temperature single-crystal experiments were done using a high temperature furnace [7] with He atmosphere. To prevent crystals from oxidation they were placed in a quartz-glass capillary and fixed with quartz wool including a piece of sodium metal as oxygen-getter at the end of the capillary, fixed into the goniometer-head, and sealed with silicone vacuum grease. Typical heating rates were in the order of 5 K/min, followed by equilibration times of about 2 min. Low temperature measurements were done using our recently built-up Fixdiff (fast in situ X-ray diffractometer), consisting of a Huber 4-circle goniometer and a mar345 image plate detector with Mo-Kα radiation. A Displex closed cycle cryostat, modified based on the ideas of [8] with a Kapton- instead of Be-shielding was used. The single-crystals were fixed with epoxy to the sample holder, a highly-conducting copper rod. Single-crystal high-pressure high-temperature experiments were done using a Diacell DXR-7H diamond-anvil cell, diamonds with 0.5 mm culet diameter, incolloy gaskets (0.15 mm sample hole diameter), and Ar as pressure-transmitting medium on the mar300 image-plate system as described above. Pressures were determined by the ruby fluorescence pressure scale (at room temperature) and gold as internal standard [9]. Quantitative reconstructions of reciprocal space were done using the program xcavate [10].

RESULTS AND DISCUSSION

Figure 1 shows reconstructed reciprocal space layers perpendicular to the five-, three-, and twofold axis of icosahedral Cd-Yb (zero layers).

![Figure 1](image)

Figure 1. Reconstructed reciprocal space layers perpendicular to a five- (a), three- (b), and two-fold (c) axis (zero layers). Total rotation angle $\phi=180^\circ$, step $\Delta\phi=1^\circ$, exposure time 600 s per frame, distance 150 mm.

The investigated crystals show sharp Bragg reflections and no significant amount of diffuse scattering. This indicates a high degree of structural order of the icosahedral quasicrystal.
Low-temperature study

In figure 2, the sums of 100 single frames obtained from a rotation of $\varphi = 50^\circ$ (step $\Delta \varphi = 0.5^\circ$) for icosahedral CdYb at room temperature and 20 K are shown. Regarding the reflections of the icosahedral single crystal, no significant differences are observable at room temperature and 20 K. No structural changes take place in this temperature range. This is in good agreement with the results of electrical resistivity and thermal conductivity measurements on this compound, that also confirm the stability of the icosahedral structure [5] at low temperatures. In both cases, the powder rings of the copper sample holder and the amorphous Kapton foil can be seen. At 20 K additional rings, belonging to solid nitrogen occur.

![Figure 2](image)

(a) room temperature (b) 20 K

Figure 2. Summarized frames collected at room temperature (a) and 20 K (b). Total rotation angle $\varphi = 50^\circ$, step 0.5 $^\circ$, distance 200 mm, 1800 s per frame. Additional powder rings result from the copper sample holder, the amorphous Kapton-foil, and solid nitrogen at 20 K.

High-temperature study

High temperature studies were done using the Laue method. As exposure times are short, this method is favored for time-critical experiments as e.g. high-temperature single-crystal studies in the laboratory. Figure 3 shows Laue diffraction pattern along a threefold axis collected as a function of temperature and annealing time.

![Figure 3](image)

Figure 3. Laue diffraction pattern taken along a threefold axis at different temperatures. Temperatures and annealing times are given besides the images. Distance 200 mm, exposure time 180 s.
During heating, the diffraction pattern shows no significant changes up to 473 K (despite a peak shift due to thermal expansion). After this temperature was held constant for 9 minutes, a radial Bragg-peak broadening was observed. Powder rings of an additional polycrystalline phase occur at 523 K. This phase could be identified as Cd. Annealing at this temperature for 17 h leads to the total disappearance of the quasicrystal reflections and an intensity gain of the textured powder rings of Cd. At 623 K the powder rings of Cd have disappeared (m.p. Cd 594 K), and untextured powder rings of CdO are present.

To summarize this experiment, it is not clear to state, whether the structural transformation is caused by the metastability of the icosahedral phase at room temperature or a partial oxidation. The structural changes at 473 K and 523 K may be caused by a reconstructive phase transition, which may be slow due to the slow kinetics of the necessary diffusion processes at these temperatures. The only residual phase at 623 K, CdO, gives strong hints for an oxidation of the sample, but obviously no other oxidation products were observed. Also no transition to an approximant phase was observed, as would have been expected according to the phase diagram and the results reported for icosahedral Cd-Ca [3]. As the solubility of Yb in Cd is negligible [2], it has to be assumed that Yb will form compounds not detectable with the current experimental setup.

**High-pressure, high-temperature study**

According to a high-pressure powder study, the icosahedral phase is stable up to 40 GPa at room temperature [6]. Starting from our results with single-crystals at low and high temperatures, it was very interesting to study for the first time the behavior of single crystalline icosahedral Cd-Yb at high pressures and high temperatures. Figure 4a shows the single-crystal and the pressure calibrants inside the sample chamber of the diamond-anvil cell. Even though the opening-angle of the diamond-anvil cell is only about 50 ° and therefore only a small part of reciprocal space is accessible, a part of a reciprocal space layer perpendicular to a fivefold axis could be successfully reconstructed. In figure 4b the reconstruction of the experimentally accessible region is shown.

![Figure 4](image)

**Figure 4.** High-pressure high-temperature study of single-crystalline icosahedral Cd-Yb. (a) Single crystal and pressure calibrants in the sample chamber (hole diameter 0.15 mm). (b) Region of the reciprocal space layer perpendicular to the fivefold axis which was experimentally accessible. (c) Detail of this layer at room temperature and ambient pressure, (b) the same region at room temperature and 9.8 GPa, and (e) this region at 873 K and ~9 GPa. \( \varphi=11 \, ^\circ, \Delta \varphi=1 \, ^\circ, \) distance 250 mm, exposure time 600 s per frame.
Compared to ambient pressure, a significant peak broadening can be observed at 9.8 GPa. As Ar was used as a pressure-transmitting medium, it can be assumed, that hydrostatic conditions are present inside the sample chamber, and therefore the peak broadening does not result from non-hydrostatic conditions. Therefore, the loading-conditions of the sample may be more important. To load the cell with Ar, it is cooled down to about 80 K and the cell is closed in liquid Ar (including initial pressurization). If we assume, that icosahedral Cd-Yb is metastable at low temperatures in combination with the application of mechanical stress (see next paragraph), the application of pressure at low temperatures may be sufficient to initialize a possible phase transition. At high pressures and high temperatures it was found to be stable (figures 4d,e). Besides the powder rings of Ar, Au and the gasket material, the reflections of the single-crystalline quasicrystal are still present. For a detailed analysis of recrystallization processes, or the shape of the reflexions as a function of pressure and temperature, further experiments have to be carried out.

**Influence of mechanical stress**

Figure 5a shows X-ray diffraction patterns of icosahedral Cd-Yb ground in a mortar at room temperature. The pattern of the same sample was taken directly after grinding and after five days.

![Figure 5. X-ray powder pattern of icosahedral Cd-Yb after grinding in a mortar at room temperature (a) and at 77 K in a ball mill (b). (a) Pattern taken directly after grinding and after five days. The arrows mark the reflections of Cd. (b) Pattern taken after 5 and 35 min of ball milling at 77 K. The arrows indicate the reflections of the icosahedral phase.](image)

After 5 days reflections of a second phase, Cd, occur in the powder pattern. No oxidation products were observed. Obviously the icosahedral phase transforms under the influence of mechanical stress at room temperature. This may indicate a low-temperature instability of the icosahedral phase. Therefore, the milling temperature was decreased and the grinding intensity increased in order to favor a possible phase transition at low temperatures. The quasicrystal was ground at 77 K in a ball mill. In figure 5b the powder pattern of icosahedral Cd-Yb ground for 5 and 35 min is shown. After 5 min milling time, the sample contains two phases, Cd and icosahedral Cd-Yb. After 35 min milling time, the reflections of the quasicrystal disappeared. Besides three weak and broad reflections (around 45° and 55° 2θ, see figure 5b), only reflections of Cd are observable. None of the known approximant structures or oxides fits to the additional reflexions.
Summary

Single crystals of icosahedral Cd-Yb are stable at low temperatures as well as at high pressures and high temperatures. Single crystals at high temperatures and powders, prepared at low temperatures decompose in the same way. The residual compounds, observable with X-ray diffraction methods, are Cd and CdO in case of single crystals at high temperatures and Cd in case of powders. The presence of CdO at high temperatures obviously indicates an oxidation during the experiment. Oxides are not observable in diffraction patterns of powders prepared at low temperatures. In both cases, no Yb-containing phases were observed in the diffraction pattern. Whether the remaining Yb forms X-ray amorphous oxides or other phases, not visible in the X-ray diffraction pattern cannot be answered. The absence of any approximant phase with a higher Cd-content than icosahedral Cd-Yb (Cd_{85}Yb_{15} or Cd_{6}Yb) and the insolubility of Yb in solid Cd [2] indicate a high mobility of Yb in the structure of icosahedral Cd-Yb, as Yb seems to be separated quantitatively from the structure, even at low temperatures.

CONCLUSIONS

The stability of icosahedral Cd-Yb was investigated in the temperature range 20 K \leq T \leq 900 K, at pressures up to about 9 GPa, and under mechanical stress at low temperatures. Single-crystalline samples show no phase transition at low temperatures. Applying mechanical stress or high temperatures yields to the same result, the formation of cadmium. This may be explained by an oxidation of the samples, implying a high mobility of Yb in the structure. On the other hand, a possible metastability of icosahedral Cd-Yb at low temperatures cannot be ruled out totally. Therefore additional experiments have to be done to clarify the behavior of icosahedral Cd-Yb at non-ambient conditions.

REFERENCES