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^{170}Yb Mössbauer study of the $YbCd_{5.7}$ binary quasi-crystal and related phases

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Abstract

^{170}Yb Mössbauer spectroscopy has been used to confirm the valence of Yb in the new binary quasi-crystalline $YbCd_{5.7}$ alloy. Comparison with other phases in the Yb–Cd phase diagram shows that the local environments of the Yb atoms are very similar.

1. Introduction

Since the original discovery of a binary quasi-crystalline phase in rapidly quenched Al–Mn alloys [1], there have been many searches for more stable examples, culminating in the demonstration that cm^3 single crystals of $Al_{70}Pd_{21.5}Mn_{8.5}$ exhibit resolution-limited diffraction peaks with mosaic spreads of less than 0.001° and a degree of perfection such that dynamical diffraction effects could be observed [2].

To date, all stable quasi-crystalline alloys found have been ternaries, and while binary quasi-crystals exist, they are all meta-stable. This changed at the end of 2000 with the identification of $YbCd_{5.7}$ as a stable, binary quasi-crystalline alloy [3]. This phase was first prepared nearly 30 years ago during an investigation of the Yb–Cd binary phase diagram [4], and despite the fact that single crystals were obtained, the structure was not determined. $YbCd_{5.7}$ is remarkable on many levels. While the RE–Cd phase diagrams are all very similar [5], only the Yb–Cd system exhibits the 1:5.7 phase. Furthermore, this phase melts congruently, making it possible to prepare single crystals. It is extremely stable, appearing as an impurity in samples of both $YbCd_6$ and $Yb_{14}Cd_{51}$ if care is not taken to accurately maintain stoichiometry.

As a first step in evaluating the structure of this remarkable new alloy, we present here a study of the local environment of the Yb atoms using ^{170}Yb Mössbauer spectroscopy. We confirm the diamagnetic state of the Yb inferred from susceptibility and show that the local Yb environments in the quasi-crystal and the two neighbouring phases are similar.

2. Experimental methods

Stoichiometric combinations of the pure metals (Cd: 99.999% and Yb: 99.9%) were melted together at 700 °C for two hours in a covered tantalum crucible under high-purity argon. The alloys were furnace cooled to about 600 °C (below their melting point), and then water quenched. As $YbCd_6$ does not melt congruently, this sample had to be further annealed at 575 °C for three hours. The melting point of YbCd (796 °C) lies above the boiling point of Cd, so this sample was prepared by first melting the constituents together at 750 °C for two hours, then heating to 810 °C for 15 minutes to fully form the YbCd phase. The sample was furnace cooled.

The materials were clearly air-sensitive, with the most Cd-rich alloys tending to discolour after a few days in air [4]; however, x-ray diffraction patterns could be obtained on powders hand-ground in air without any apparent problems. The exceptions were $YbCd_2$ and YbCd which both showed significant changes (precipitation of metallic cadmium was seen by x-ray diffraction) within an hour of exposure to air. These materials were therefore ground under argon in a glove box and then transferred to an evacuated enclosure with a Kapton window for the diffraction measurements. Powder x-ray diffraction measurements, shown in figure 1, were made using Cu Kα radiation on an automated diffractometer.

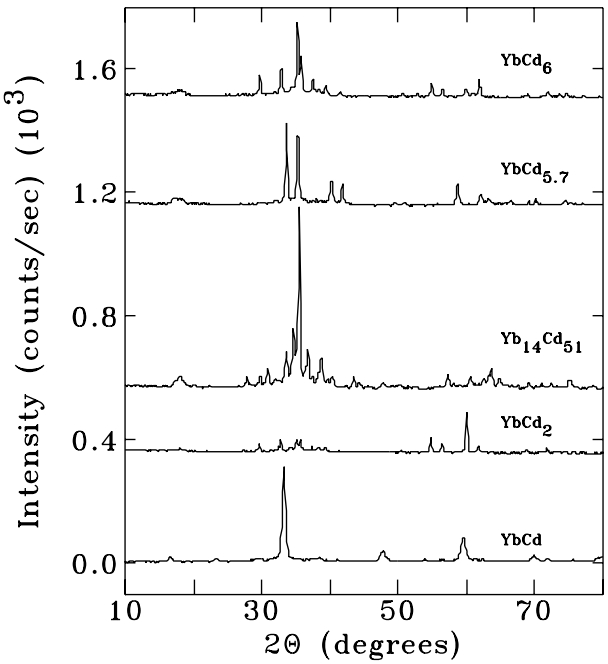

Figure 1. Cu Kα x-ray diffraction patterns for the five Yb–Cd alloys studied here.

A 10 mCi ^{170}Tm source was prepared by neutron activation of ∼25 mg of Tm as a 10 wt% alloy in aluminium. The source and sample were mounted vertically in a helium-flow cryostat and the drive was operated in sine mode. The 84.25 keV γ-photons used for the ^{170}Yb Mössbauer spectroscopy were isolated from the various x-rays emitted by the source using a high-purity Ge detector. Simultaneous calibration of the spectrometer was achieved by mounting a ^{57}Co source on the top of the drive and recording the ^{57}Fe Mössbauer spectrum of an α-Fe foil. With both sample and source at 4.5 K, we observed a linewidth of 1.16(5) mm s^{-1} for

the YbCd sample. Spectra were fitted using a non-linear least-squares minimization routine. Line positions and intensities were derived from an exact solution to the full Hamiltonian. Isomer shifts are quoted relative to ^{170}Yb in the $TmAl_2$ source.

3. Results and discussion

The four congruently melting phases in the Yb–Cd binary phase diagram have been prepared, along with the cubic approximant phase $YbCd_6$. Cu Kα x-ray diffraction patterns confirmed that single-phased samples of each of the five materials under study were obtained and that the patterns matched those of the published phases [4,5]. The pattern for the quasi-crystalline $YbCd_{5.7}$ sample in figure 1 exhibits the characteristic structure typical of most quasi-crystals. The broad feature below $2\theta = 20^\circ$, seen in the patterns of those samples stable enough to undergo measurements in air, was attributed to Yb_2O_3 formed by surface oxidation. Severe oxidation of $YbCd_2$ and YbCd was signalled by the presence of strong reflections from metallic Cd. Making measurements in the sealed enclosure eliminated this problem and also avoided the formation of Yb_2O_3. Table 1 summarizes the structures, lattice parameters and Yb sites in the five compounds studied here. Only YbCd has a Yb site with high enough symmetry ($m\bar{3}m$) to have zero electric field gradient (efg).

Table 1. Summary of crystal structures and Yb site properties in the Yb–Cd phases studied here.

Compound	Structure type/ space group	Lattice parameters (Å)	Ytterbium site	Site symmetry	Volume (Å^3)
YbCd	CsCl $Pm\bar{3}m$	$a = 3.8086$	1b	$m\bar{3}m$	33.4
$YbCd_2$	$MgZn_2$ $P6_3/mmc$	$a = 5.991$ $c = 9.596$	4f	$3m$.	35.7
$Yb_{14}Cd_{51}$	$Ag_{51}Gd_{14}$ $P6/m$	$a = 13.441$ $c = 9.655$	2e 6j 6k	6 . . m . . m . .	33.9 36.1 35.9
$YbCd_{5.7}$	QC	—	—	—	—
$YbCd_6$	$YbCd_6$ $Im\bar{3}$	$a = 15.638$	24g	m . .	35.9

The ^{170}Yb Mössbauer spectra measured for the five alloys at 4.5 K are shown in figure 2. No contamination by Yb_2O_3 was observed in the spectrum of any sample, confirming that no more than slight surface oxidation occurred during handling, even in the cases of $YbCd_2$ and YbCd which had to be handled in a glove box during mounting.

The spectrum of YbCd is well fitted by a single sharp Lorentzian ($\Gamma = 1.16(5)$ mm s^{-1}), consistent with the high symmetry of the single Yb site present in the structure (table 1). By contrast, however, single-line fits to the other alloys yield linewidths of $\sim$1.5 mm s^{-1}. Furthermore, such fits fail to reproduce the slight asymmetry present in the spectra. Inclusion of a small quadrupole splitting $eQV_{zz} \sim 2.4$ mm s^{-1} visibly improved the fits, and led to fitted linewidths of $\sim$1.2 mm s^{-1} in each case. These linewidths are consistent both with that obtained for YbCd, where the efg is expected to be zero, and also with linewidths obtained for standard materials. Unfortunately, the observed efg is too small to permit its sign to be determined. We did not detect any additional broadening associated with the three distinct sites in $Yb_{14}Cd_{51}$. No attempt was made to refine an asymmetry parameter. The trends in the fitted parameters are summarized in figure 3.

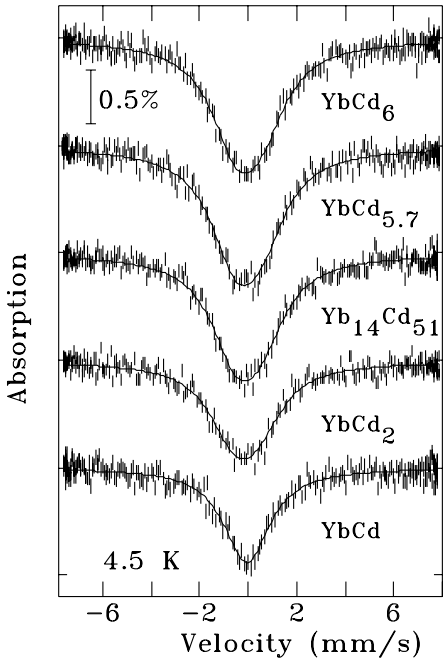

Figure 2. ^{170}Yb Mössbauer spectra of the five Yb–Cd alloys studied here. The solid lines are fits as described in the text.

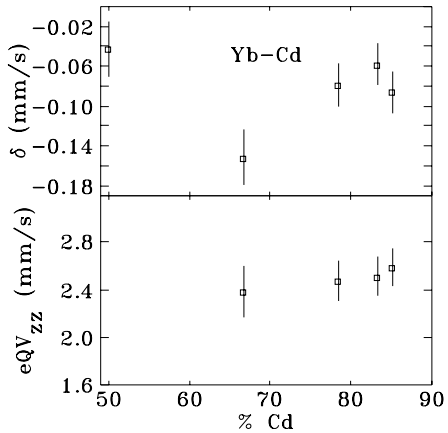

Figure 3. Fitted isomer shifts (δ) and quadrupole splittings (eQV_{zz}) for the Yb–Cd alloys at 4.5 K.

The isomer shifts are fully consistent with the ytterbium being present as diamagnetic Yb^{2+} in all of these alloys [6], confirming the magnetic susceptibility results reported by Palenzona [4]. As Yb^{2+} is a spherical ion with a closed 4f shell, there is no magnetic moment, and no local contribution to the electric field gradient at the nucleus. Observed quadrupole splittings are due to the effects of the first neighbours. The spectra of the quasi-crystalline $YbCd_{5.7}$ alloy and those of the two neighbouring phases $Yb_{14}Cd_{51}$ and $YbCd_6$ are identical within error, indicating that the local environments of the Yb in these complex structures are quite similar.

The temperature dependence of the spectral area for the quasi-crystalline $YbCd_{5.7}$ alloy indicates an effective Debye temperature of 158 ± 8 K, consistent with heat capacity measurements which yield $\sim$140 K [7].

4. Conclusions

Ytterbium is clearly divalent in all of the alloys studied here. The high symmetry of the Yb site in YbCd allows us to establish the unperturbed linewidth for this alloy system and thus confirm that the additional broadening seen in the other alloys is indeed due to the effects of an electric field gradient. The consistency of the measured efg in the four Cd-rich alloys suggests that, within the resolution of ^{170}Yb Mössbauer spectroscopy, the local environments of the Yb atoms in these alloys are quite similar.

Acknowledgments

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