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Physical properties of the quasicrystal $\text{YbCd}_{5.7}$ and its approximant YbCd_6

S K Dhar^{1,3}, A Palenzona², P Manfrinetti² and S M Pattelwar¹

¹ CMP and MS, TIFR, Homi Bhabha Road, Mumbai, 400 005, India

² INFN and Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso 31, I-16146 Genova, Italy

E-mail: sudesh@tifr.res.in

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Abstract

We have measured the magnetization, low-temperature heat capacity and electrical resistivity of the binary quasicrystal $\text{YbCd}_{5.7}$ and its crystalline approximant, cubic YbCd_6 . Magnetization data reveal that Yb ions are divalent in both compounds. The coefficient of the linear term in the heat capacity, γ , is 51 and 7.5 $\text{mJ mol}^{-1} \text{K}^{-2}$ in YbCd_6 and $\text{YbCd}_{5.7}$, respectively. The heat capacity data thus reveal a significant reduction in the electronic density of states in the quasicrystalline phase. However, the Debye temperatures of the two compounds are comparable; 144 and 138 K, respectively. The electrical resistivity of YbCd_6 shows typical metallic behaviour while the resistivity of $\text{YbCd}_{5.7}$, larger than that of YbCd_6 , is characterized by a negative temperature coefficient below 300 K with a peak around 50 K.

1. Introduction

Quasicrystals are a fascinating new class of compounds in the chemistry and physics of the solid state. They have long-range orientational order but lack periodic translational order. The synthesis of the first quasicrystal, an alloy of aluminium and manganese, was reported by Shechtman *et al* in 1984 [1]. Later, many other quasicrystals were identified especially in ternary or higher-order systems, the majority of them being either icosahedral (i) or decagonal (d) alloys. Recently, Tsai *et al* [2] showed that $\text{YbCd}_{5.7}$ is a new thermodynamically stable quasicrystal formed by only two metallic elements, exhibiting three-dimensional icosahedral symmetry. It is, therefore, a good candidate to choose if one wishes to study and understand characteristic features of quasiperiodic structures. Further, a comparison of its physical properties with those of the adjacent YbCd_6 phase, which has cubic crystal structure, should be interesting. The Yb–Cd phase diagram was studied many years ago by Palenzona [3],

³ Author to whom any correspondence should be addressed.

and YbCd_6 can be considered as an approximant to the quasicrystal $\text{YbCd}_{5.7}$. We present in this paper a study of the magnetization, heat capacity and electrical resistivity of YbCd_6 and $\text{YbCd}_{5.7}$.

2. Experimental procedure

Commercial Yb of 99.9 wt% nominal purity and Cd of 99.999 wt% nominal purity were used to prepare YbCd_6 and $\text{YbCd}_{5.7}$. The compounds were prepared by heating weighed amounts of Yb and Cd taken in the form of turnings, a total weight of about 5 g each, in Ta crucibles closed by welding under pure argon in a high-frequency induction furnace. The samples were remelted twice after the crucible was flipped upside down to ensure homogenization. It is known from Yb–Cd phase diagram that $\text{YbCd}_{5.7}$ melts congruently at 636 °C while YbCd_6 forms peritectically at 614 °C [3]. Therefore, YbCd_6 was annealed in a Ta crucible closed in a quartz ampoule under vacuum at 580 °C for six days, while $\text{YbCd}_{5.7}$ was used in the as-cast condition. Specimens for metallographic examination were prepared by standard methods and checked by optical and electron microscopy (a SEM equipped with a microprobe EDX). X-ray powder patterns were obtained by both a powder diffractometer and a Guinier camera, with Cu $K\alpha$ radiation and pure Si as the internal standard ($a = 5.4308 \text{ \AA}$). The freshly polished surfaces of both samples have a shining metallic lustre, but they are susceptible to the formation of a superficial dull oxide layer. Resistivity measurements were carried out by the four-probe dc method; magnetization was measured in a Quantum Design SQUID magnetometer. Heat capacity data were collected using the semi-adiabatic, heat pulse method.

3. Results

Metallographic examination showed that both samples are silvery, homogeneous single-phase alloys with less than 1% free Cd. The x-ray powder diffraction patterns of $\text{YbCd}_{5.7}$ and YbCd_6 are shown in figure 1. For $\text{YbCd}_{5.7}$, the spectrum is similar to that reported by Guo *et al* (figure 1 of [5]) for their as-cast quasicrystalline sample of $\text{Cd}_{85.1}\text{Yb}_{14.9}$. The broad feature around 20° is due to the sample holder. The lattice parameters, as obtained from the Guinier pattern, are $a_R = 5.686(6) \text{ \AA}$ and $a = 15.636(8) \text{ \AA}$ for the icosahedral phase $\text{YbCd}_{5.7}$ and the cubic phase YbCd_6 , respectively. These values agree well with previous data [3, 5] and confirm the relation between the lattice value of a quasicrystal phase and its approximant, i.e. $a = a_R(4 + 8/\sqrt{5})^{1/2}$ [5]. It may be of academic interest to note that in [3] a lattice constant of 108 Å, nineteen times the above value of a_R , was derived for a pseudocubic cell of $\text{YbCd}_{5.7}$ by rotating and Weissenberg photographs (single crystal).

Figure 2 shows the magnetic susceptibilities of YbCd_6 and $\text{YbCd}_{5.7}$ measured in an applied field of 20 kOe. The inset depicts plots of isothermal magnetization measured up to 55 kOe at 1.7, 5 and 10 K. The susceptibility is diamagnetic at 300 K with a value of -2.14×10^{-5} and $-8.32 \times 10^{-5} \text{ emu mol}^{-1}$ in YbCd_6 and $\text{YbCd}_{5.7}$, respectively. As the temperature is decreased, the susceptibility becomes paramagnetic below 240 and 80 K in the two compounds, respectively, but its value remains low. The diamagnetic susceptibility at higher temperatures and low paramagnetic susceptibility at lower temperatures show unambiguously that Yb ions in both the compounds do not possess any magnetic moment and are in the divalent $4f^{14}$ ($J = 0$) state. For YbCd_6 this is in conformity with the lattice constant which shows an appreciable deviation from the value based on the normal lanthanide contraction. The expanded lattice of YbCd_6 indicates a divalent state of Yb as the ionic radius of Yb^{2+} is greater than that of $\text{Yb}^{3+}(4f^{13})$. In the case of $\text{YbCd}_{5.7}$, the very existence of its quasicrystalline state has been

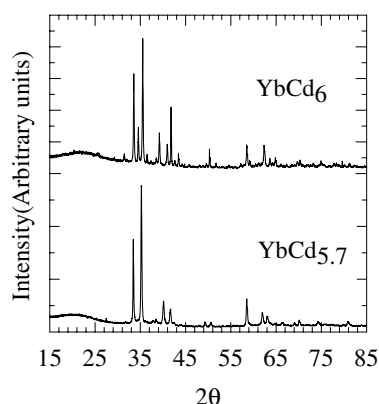


Figure 1. The x-ray diffraction patterns of YbCd_6 and $\text{YbCd}_{5.7}$.

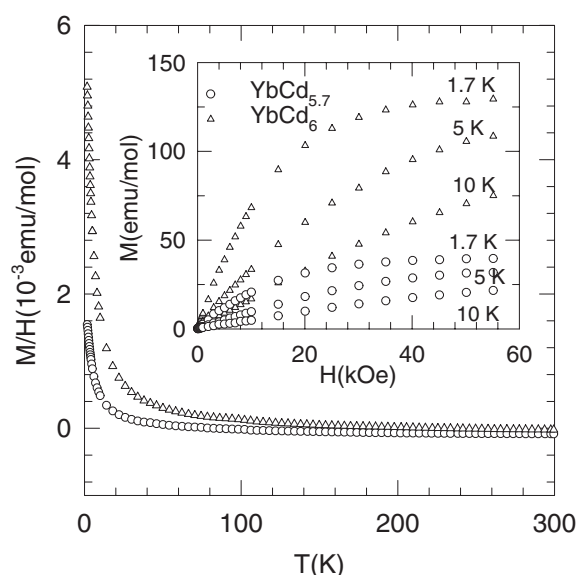


Figure 2. Magnetization versus temperature between 1.7 and 300 K in an applied field of 20 kOe in YbCd_6 and $\text{YbCd}_{5.7}$. The inset shows the magnetization up to 55 kOe at 1.7, 5 and 10 K.

linked to the divalent character of Yb, as the other trivalent rare-earth ions do not form the quasicrystalline phase. A situation similar to that found in the Yb–Cd system is also present in the Ca–Cd system [4] where again we have two compounds CaCd_6 and $\text{CaCd}_{5.7}$, isotypic with those of the corresponding Yb analogues. The ionic radius of divalent calcium is close to that of divalent ytterbium, and $\text{CaCd}_{5.7}$ is another representative, though with reduced thermodynamical stability, of the quasicrystal state [5]. The sharp increase in the susceptibility of YbCd_6 and $\text{YbCd}_{5.7}$ at lower temperatures is most probably not intrinsic and may be attributed to the presence of trace amounts of parasitic magnetic impurities. The curvature in the magnetization at 1.7 and 5 K (inset, figure 2) implies that the intrinsic value of the susceptibility of YbCd_6 and $\text{YbCd}_{5.7}$ at low temperatures is less than that observed in the applied field of 20 kOe.

Figure 3 shows the heat capacity, C , in the form of C/T versus T^2 . The data were recorded from 2 to 20 K and are plotted up to 10 K in the figure. A linear dependence of C/T

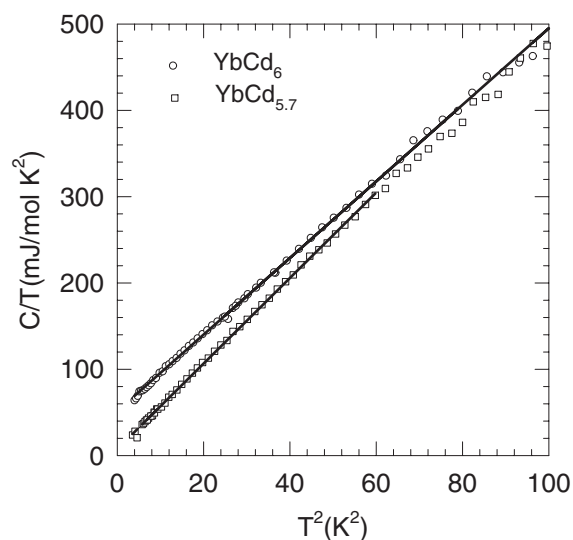


Figure 3. The heat capacity, C , of YbCd_6 and $\text{YbCd}_{5.7}$ in the form of C/T versus T^2 . The line drawn through the data points is a least-squares fit to the expression $C/T = \gamma + \beta T^2$.

on T^2 is observed up to 9 and 8 K in YbCd_6 and $\text{YbCd}_{5.7}$, respectively. The heat capacity of YbCd_6 was measured twice with the sample mass differing by a factor of nearly three in the two runs. Least-squares fits of the two independent data sets of YbCd_6 to the expression $C/T = \gamma + \beta T^2$, where γ and β are the Sommerfeld coefficient and the coefficient of the lattice (phonon) heat capacity, respectively, give $\gamma = 51.4$ and $50.3 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\beta = 4.438$ and $4.592 \text{ mJ mol}^{-1} \text{ K}^{-4}$ (we define 'mol' here as a molecular mole). The value of the Debye temperature, θ_D , can be derived from β using the relationship $\theta_D^3 = 1.9436 \times 10^6 n / \beta$ where n is the number of atoms per formula unit (7 in YbCd_6 and 6.7 in $\text{YbCd}_{5.7}$). We obtain $\theta_D = 145.2$ and 143.6 K from the two sets of data. It will be noticed that the variation in the values of γ and θ_D is to within 2%. This is typically the accuracy of our heat capacity set-up. For quasicrystal $\text{YbCd}_{5.7}$ we get $\gamma = 7.5 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\beta = 4.954 \text{ mJ mol}^{-1} \text{ K}^{-4}$. From β we derive a value of 138 K for the Debye temperature of $\text{YbCd}_{5.7}$. The similarity of the magnitudes of θ_D in the two compounds is quite plausible, as the two have nearly the same composition and YbCd_6 is the crystalline approximant of quasicrystal $\text{YbCd}_{5.7}$. On the other hand, there is an appreciable difference between the γ -values of the two compounds, pointing to a marked difference in the electronic density of states at the Fermi level.

The thermal variation of the resistivity of YbCd_6 , plotted in figure 4, shows typical metallic behaviour. It decreases monotonically with the decrease of temperature with $\rho(300 \text{ K})/\rho(4.2 \text{ K})$ nearly equal to 4. A noteworthy feature of the resistivity is the anomalous drop occurring near 110 K, shown on an enlarged scale in the inset. The sample was thermally cycled up and down around 110 K a few times and its resistivity measured. We find that the resistivity is reversible and does not show any hysteresis. The sample was given a mild anneal at 450°C for five days and its resistivity remeasured. We found that the resistivity was practically unchanged. The drop at 110 K cannot be ascribed to a magnetic transition as the Yb ions in YbCd_6 do not have a magnetic moment owing to their divalent state. One may invoke change in the valence of Yb ions as the cause of the anomaly, but we do not see any signature of the valence transition in the susceptibility data. In order to check whether the behaviour around 110 K is due to a change in the crystal structure, we recorded the x-ray

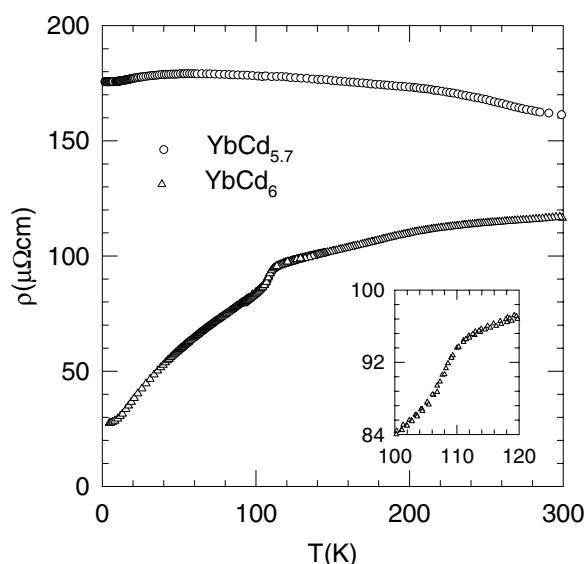


Figure 4. The electrical resistivity, ρ , of YbCd₆ and YbCd_{5.7} between 4.2 and 300 K.

diffraction spectrum at 77 K. A comparison with the spectrum taken at room temperature did not, however, reveal any change in crystal symmetry. Therefore, at present the origin of the feature at 110 K is not clear to us. The resistivity of quasicrystal YbCd_{5.7}, also shown in figure 4, is qualitatively very different from that of YbCd₆. It shows a negative temperature coefficient from 300 K down to nearly 50 K. The resistivity decreases at lower temperatures and becomes nearly temperature independent, within the scatter of the data, below 8 K. The ratio $\rho(300 \text{ K})/\rho(4.2 \text{ K})$ is about 0.92.

The heat capacity and the electrical resistivity data bring out the difference in the physical properties of YbCd₆ and the quasicrystal YbCd_{5.7}. The Sommerfeld coefficient γ of YbCd₆ is nearly seven times that of YbCd_{5.7}, indicating an appreciably lower electronic density of states at the Fermi level in YbCd_{5.7}. Therefore, the Pauli paramagnetic susceptibility, which is proportional to the density of states, will be lower in the quasicrystalline YbCd_{5.7}. On the other hand, the temperature-independent diamagnetic contributions to the susceptibility due to the filled shells of Yb and Cd will be nearly equal in the two compounds. Consequently, we observe a larger (net) diamagnetic susceptibility in YbCd_{5.7} compared to that in YbCd₆ at 300 K. Typically Pauli susceptibility of simple metals is nearly temperature independent. But a weak variation of susceptibility with temperature is seen in both compounds which is more pronounced as a 'Curie tail' at low temperatures. At higher temperatures the weak temperature variation results in (net) paramagnetic susceptibility below 240 and 80 K, respectively, in YbCd₆ and YbCd_{5.7}. Using the relationship based on the free-electron model between χ_0 and γ : $\chi_0 (\text{emu mol}^{-1}) = 1.3715 \times 10^{-5} \gamma (\text{mJ mol}^{-1} \text{K}^{-2})$ we obtain $\chi_0 = 7 \times 10^{-4}$ and $1 \times 10^{-4} \text{ emu mol}^{-1}$ for $\gamma = 51.4$ and $7.5 \text{ mJ mol}^{-1} \text{K}^{-2}$ in YbCd₆ and YbCd_{5.7}, respectively. A value of $-3.4 \times 10^{-4} \text{ emu mol}^{-1}$ is derived for the diamagnetic susceptibility using the approximate relationship $\chi_{\text{dia}} = 10^{-6} Z$, where Z is the atomic number per formula unit. χ_0 and χ_{dia} are seen to be comparable. The value of χ at 1.7 K (in an applied field of 20 kOe) in the two compounds is an order of magnitude larger than χ_0 . While χ_0 may be intrinsically weakly temperature dependent, the pronounced increase in the susceptibility at low temperatures is mostly of extrinsic origin. We believe that the low-temperature susceptibility is dominated

by the presence of trace, parasitic magnetic impurities. The presence of even 0.1% of Yb_2O_3 (Yb ions are in the trivalent state in Yb_2O_3 and possess a magnetic moment) in the samples would result in an impurity susceptibility of $1.5 \times 10^{-3} \text{ emu mol}^{-1}$ at 1.7 K. We have already mentioned that the samples are susceptible to superficial oxidation; the oxide or other rare-earth ions may be present as trace impurities even in the Yb metal used in the sample preparation.

The γ -value for the known quasicrystals, mostly ternaries and quaternaries, is typically $\sim 1 \text{ mJ mol}^{-1} \text{ K}^{-2}$, where 'mol' refers to atomic mole [6]. Thus, γ for binary $\text{YbCd}_{5.7}$ as derived from our data above is comparable to that of other known quasicrystals. Experiments on stable, phase pure quasicrystals have shown that they possess an unusually high electrical resistivity which in some cases exceeds the inverse of the minimum metallic conductivity [6]. In many systems, such as $\text{Al}_5(\text{Li}_{1-x}\text{Mg}_x)_{3.5-4}\text{Cu}$ ($0 \leq x \leq 1$) i alloys, the temperature dependence of the resistivity is seen to change systematically, analogously to that for the corresponding amorphous alloys [7]. It is seen that as γ decreases, ρ increases and the temperature coefficient changes from positive to negative. For some intermediate values, ρ initially increases below 300 K and exhibits a peak at lower temperature, similar to what is seen in $\text{YbCd}_{5.7}$. The large resistivity ρ and the low value of γ in quasicrystals have been qualitatively ascribed to the presence of a pseudo-gap in the electron density of states. Our data indicate a sizable reduction in the electronic density of states at the Fermi level in the quasicrystal $\text{YbCd}_{5.7}$ compared to the crystalline approximant YbCd_6 . Finer details of the electronic structure in quasicrystal $\text{YbCd}_{5.7}$ will have to be probed further by using other experimental techniques. They may also shed some more light on the relative roles of the complex local atomic order and the long-range quasiperiodicity in shaping the unusual behaviour of the quasicrystals.

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