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A neutron diffraction study of the phase transition in Pd_2TiIn

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Abstract. Powder neutron diffraction measurements have been undertaken on Pd_2TiIn over the temperature range 4–300 K. Previous measurements of the bulk magnetic properties indicated a magnetic transition in the neighbourhood of 110 K. The neutron measurements reveal a structural phase transition at 92 K. The transition appeared to be of first order, and no evidence was found of any long-range magnetic order below 92 K. However, the existence of ferrimagnetic order, involving the Pd and Ti atoms, could not be ruled out. The results are discussed in terms of the stability of the magnetic moment and the presence of spin fluctuations.

1. Introduction

Recent measurements of the bulk susceptibility of Pd_2TiIn indicated a phase transition in the neighbourhood of 110 K [1]. The transition was also confirmed by resistivity measurements. On the basis of the susceptibility results, it was suggested that below 110 K the compound became antiferromagnetic. Above the transition temperature, the susceptibility had a Curie-Weiss dependence yielding an effective paramagnetic Bohr magneton number of $4.9\mu_B$ per Pd_2TiIn formula unit. This result was surprising, since none of the constituent elements is themselves magnetic. The calculated values of the quantity $\sqrt{g^2S(S+1)}$ are 1.73 for Ti^{3+} and 2.83 for Ti^{2+}. Therefore, in order to try to establish the nature of the ground state in this compound, a powder neutron diffraction study was initiated. The results of this investigation are reported here.

2. Experimental details

Details of the bulk magnetic measurements have been reported elsewhere [1]. The bulk susceptibility as obtained by SQUID magnetometry is reproduced in figure 1. A broad peak in the susceptibility occurs around 110 K, suggesting an ordered magnetic ground state. The neutron measurements were carried out using a multidetector diffractometer located on a thermal beam in the Siloé reactor of the CENG in Grenoble. A neutron wavelength of 2.499 Å was employed and diffraction patterns were recorded over a 2θ range of 5–85° in steps of 0.01°. The powder sample was the same as used in previous work [1]. It was loosely packed in a hollow double cylinder sample holder of wall thickness 0.5 mm in

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order to minimize the effects of absorption, with a sample volume of ~ 1 cm^3. The powder specimen was held in place by quartz wool plugs, and located in an He flow cryostat. Several patterns were recorded at a series of stable temperatures between 4 and 300 K with the temperature being indicated by an Si diode in thermal contact with the specimen. The diffraction patterns obtained at 4 and 300 K are shown in figure 2. Each diffraction pattern was analysed using a Rietveld refinement method capable of considering both nuclear and magnetic scattering.

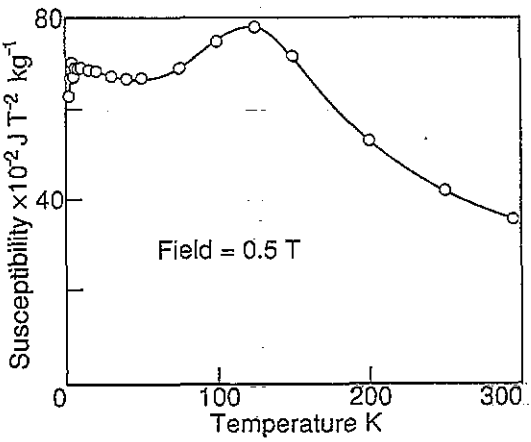

Figure 1. The magnetic susceptibility of Pd_2TiIn as a function of temperature.

3. Results

Between 300 and 92 K the neutron diffraction patterns are all very similar and consistent with single-phase $L2_1$ structure (see table 1). Over this temperature range the SQUID measurements indicate that the compound is paramagnetic with a Curie–Weiss susceptibility. A profile refinement considering only nuclear scattering confirmed that the compound was atomically ordered in the $L2_1$ structure with space group $Fm\bar{3}m(O_h^5)$. In addition to those reflections with *hkl* all even or odd, associated with $L2_1$ structure, the patterns contained a (110) reflection from the V sample holder and some scattering emanating from the quartz wool retaining the powder specimen.

Using the following nuclear scattering lengths: $b_{Ti} = -0.33 \times 10^{-12}$ cm, $b_{In} = 0.406 \times 10^{-12}$ cm and $b_{Pd} = 0.591 \times 10^{-12}$ cm excellent agreement was obtained between the observed and calculated profiles using the parameters given in table 1. The reliability factor of the refinement

$$R = \frac{\sum |(I_{obs} - I_{calc})|}{I_{obs}}$$

was 2%, indicating a highly ordered $L2_1$ structure. The results of the refinement are shown in figure 2. The full curve in figure 2 represents the calculated pattern and the dots the

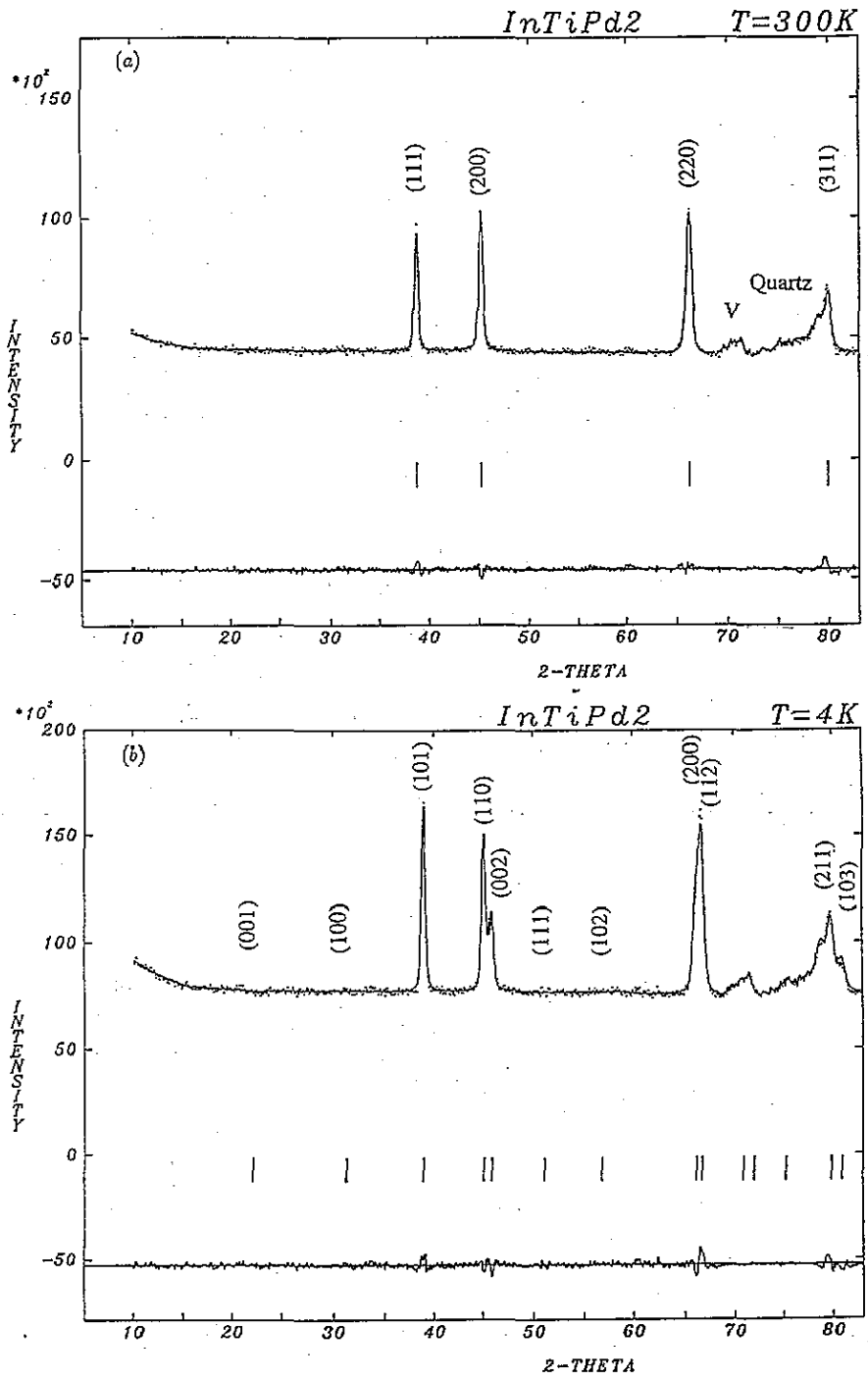

Figure 2. (*a*) The upper dotted and solid lines represent the observed and calculated diffraction patterns for Pd_2TiIn at 300 K. Below the diffraction pattern the positions of the Bragg peaks are indicated by short vertical lines and the lowest curve represents the difference between the observed and calculated profiles. (*b*) The upper dotted and solid lines represent the observed and calculated diffraction patterns for Pd_2TiIn at 4 K. Below the diffraction pattern the positions of the Bragg peaks are indicated by short vertical lines and the lowest curve represents the difference between the observed and calculated profiles.

observed pattern. Below the diffraction pattern the positions of the Bragg peaks are indicated by short vertical lines and the lowest curve represents the difference between the observed and calculated profiles. At room temperature the cell parameter was refined to 6.406(1) Å.

Below 92 K, a change appears in the diffraction pattern in which all the (h00) and (hh0) reflections are split, while the (hhh) reflections remain unchanged. (While in the figure shown here only one reflection of each set is present, the above generalization is supported by preliminary neutron diffraction experiments over a much wider range of scattering angles.) In fact, the cubic (200) reflection gives rise to two peaks with an intensity ratio of 2:1, which could be indexed as (110) and (002) assuming the tetragonal crystal structure. The lattice parameters of the cubic and tetragonal structures are related by $a_t = a_c/\sqrt{2}$ and $c_t = c_c$. Likewise the (220) cubic reflection is split into two peaks, with intensity ratio 1:2, which can be indexed as (200) and (112). The low-temperature ($T < 90$ K) patterns are then characteristic of a crystallographic distortion from a face centred cubic structure to a body centred tetragonal one. The corresponding space group is $I4/mmm(D_{4h}^{17})$. The cell parameters at 4 K are $a_t = 4.5383(9)$ Å and $c_t = 6.3268(9)$ Å giving $c_t/\sqrt{2}a_t = 0.986$.

Table 1. Atomic Positions in the two crystallographic space groups for the face centred cubic $Fm\bar{3}m$ and the body centred tetragonal $I4/mmm$ structures.

Face-centred cubic ($Fm\bar{3}m$)				Body centred tetragonal ($I4/mmm$)			
Atom	Site	Site symmetry	Atomic positions	Atom	Site	Site symmetry	Atomic positions
Ti	4a	$m\bar{3}m$	(0, 0, 0)	Ti	2a	$4/mmm$	(0, 0, 0)
In	4b	$m\bar{3}m$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	In	2b	$4/mmm$	$(0, 0, \frac{1}{2})$
Pd	8c	$\bar{4}3m$	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	Pd	4d	$\bar{4}m2$	$(\frac{1}{2}, 0, \frac{1}{4})$
			$(\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$				$(\frac{1}{2}, 0, \frac{1}{4})$

As shown in table 1, the 8c site of the Pd atoms in the face centred cubic structure becomes the 4d site in the tetragonal phase. The crystallographic parameters obtained by profile refinement of the 4 K data are reported in table 1. In the tetragonal phase, the agreement between the calculated nuclear structure and the observed pattern is excellent, with a reliability in the least-squares refinement of $R = 2.5\%$.

The thermal variation of the lattice parameters determined from the neutron diffraction experiment is shown in figure 3 and the variation of the unit cell volume as a function of temperature is shown in figure 4. At 92 K there is a huge discontinuity in the lattice parameters, consistent with a first-order transition. The a parameter is seen to increase abruptly, $\Delta a/a = 0.35\%$, while the c parameter decreases, $\Delta c/c = 0.68\%$. In contrast, the volume does not show any anomaly at 92 K (figure 4).

Owing to the peak in the susceptibility around 110 K, the possibility of magnetic scattering was also considered below 92 K. However, below the transition temperature of 92 K the neutron diffraction patterns did not show evidence of long-range antiferromagnetic order, i.e., there were no additional magnetic peaks. A lower limit of the size of the order magnetic moment is set to $1\mu_B$ per formula unit. Due to the extinction conditions associated with the body centred tetragonal structure ($h + k + l = 2n$), the (001), (100), (111) and (102) reflections are systematically absent. The absence of these peaks leads to the following conclusions: either there is no long-range antiferromagnetic order with a significant moment, or there is only a ferromagnetic or ferrimagnetic coupling of magnetic

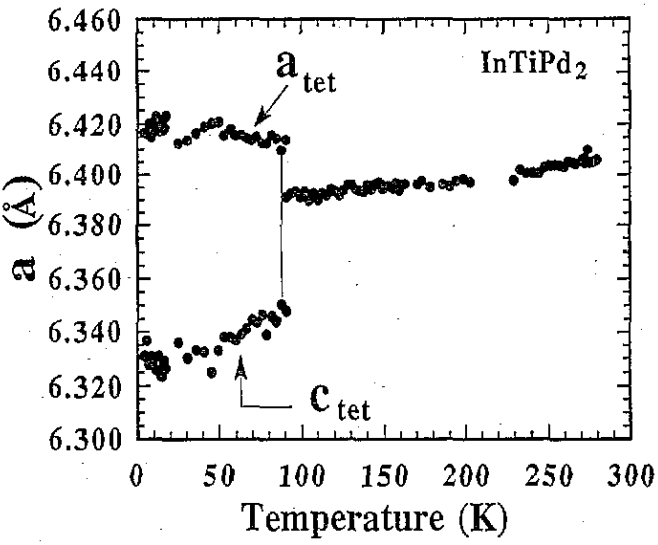

Figure 3. *The thermal variation of the lattice parameters of Pd_2TiIn showing a discontinuity at* 92 K.

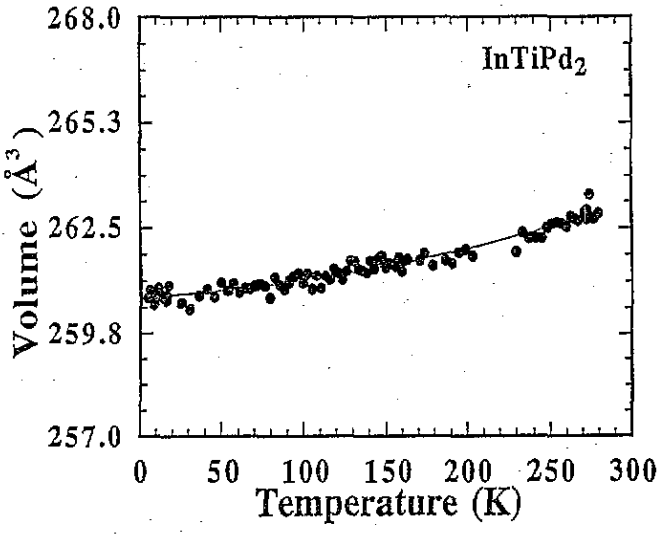

Figure 4. The variation of unit cell volume as a function of temperature. It may be noted that there is no apparent change in volume at 92 K.

moments on two crystallographically different sites, i.e. between Pd and Ti moments. The possibility of ferri- or ferromagnetic order would give a small contribution to the intensity of the nuclear Bragg reflections (011), (110), (002), (200) and (112). Such a possibility is entirely consistent with the occurrence of a very weak ferromagnetic component observed in the magnetization measurements. In a powder experiment a small magnetic contribution

to intense nuclear reflections would not easily be resolved, and single-crystal measurements using polarized neutrons would be highly desirable to resolve the issue.

4. Discussion

A lattice distortion is often observed with the onset of long-range magnetic order, for example in the $Pd_2Mn(InSn)$ [2] and $(AgPd)_2MnIn$ [3] systems. In these systems the lattice distortion originates from a magnetostrictive interaction with the distortion reflecting the configurational symmetry of the magnetic structure and proportional to the size of the ordered moment. Although on the basis of the neutron results the origin of the structural phase transition in Pd_2TiIn is different, one would expect that if at low temperatures the system ordered antiferromagnetically, it would have a tetragonal magnetic structure. If it were assumed that the moment was solely associated with the Ti atoms, then this could only mean an antiferromagnetic structure of the first kind associated with the face centred cubic lattice [4]. Clearly the low-temperature neutron results do not support this contention. Nor is there any evidence, on the basis of the powder data, of a substantial moment at low temperatures; yet on the basis of the susceptibility measurements the Curie–Weiss behaviour indicates an effective Bohr magneton number of $4.9\mu_B$ per formula unit. If this were truly a local moment system, then the ground state moment per Ti would be $P_{\text{eff}}^2 = \mu(\mu + 2)$ with $\mu = 4\mu_B$. Clearly such a moment would be visible in the neutron diffraction experiment. Furthermore, if the moment were just restricted to the Ti atoms, then since they are separated by more than 4.6 Å we would expect them to behave as a local moment system, as is the case for Mn in Pd_2MnIn [5], and observe the $4\mu_B$ in the ground state. Since Pd is highly polarizable it is possible that a ferrimagnetic order prevails below the transition temperature, giving rise to a small amount of scattering located on the nuclear Bragg peaks. Observation of magnetic scattering will provide information on the wave function of those electrons giving rise to the magnetism. The spatial spread is reflected in the radial extent of the magnetic form factor. For truly de-localized (free electron) magnetism, the magnetic form factor will be sharply peaked at a scattering vector of $q = 0$. A localized magnetic density in real space results in an increased extent of the magnetic form factor in reciprocal space. It is argued here that, depending upon the localization of the magnetic electrons, the magnetic Bragg intensity may be expected to be intrinsically weak, even if simultaneously connected with a large magnetic moment. It is quite clear that Pd_2TiIn cannot be considered a local moment system of fixed amplitude on the Ti atoms. As was conjectured in our original paper [1], the origin of the Curie–Weiss susceptibility at high temperatures and the large effective moment may lie in the presence of spin fluctuations. The structural phase transition observed at 92 K may therefore have its origin in the instability of the local moment. Although there is no anomaly observed in the atomic volume at the phase transition, one would not necessarily be expected since the $k = 0$ mode associated with the volume change does not necessarily couple to the propagation vector characterizing the symmetry of the magnetic structure.

The static susceptibility measurements point to an antiferromagnetic ground state. However, more detailed analysis of these results suggests a more complicated ground state. This may be seen in figure 5, where the data are represented in the form of Arrott plots, namely σ^2 versus B_0/σ. Here σ is the magnetic moment normalized to the mass of the sample. Whilst the isotherms above 92 K move towards lower B_0/σ values as the transition is approached from above, the tendency is reversed at lower temperatures. This behaviour

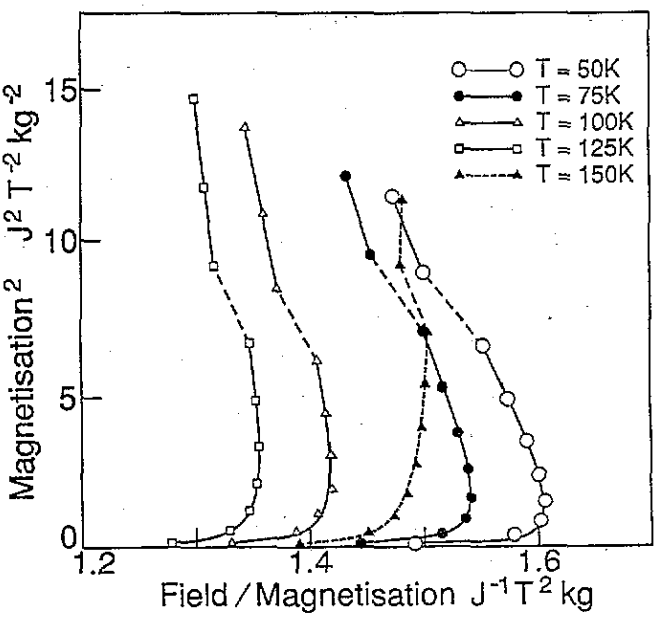

Figure 5. Arrott plots for Pd_2TiSn showing isotherms in the region of the phase transition at 92 K. Note the change of character between 125 K and 150 K. Below 125 K the isotherms move to smaller B_0/σ values, whereas above this temperature they move to higher values.

is entirely consistent with the onset of antiferromagnetic order below 92 K. However, it may be seen that the functional form of the magnetic isotherms is complicated and remote from the linear behaviour expected for collinear antiferromagnetism. This non-linear behaviour is entirely consistent with the onset of ferrimagnetic order, which would arise if both the Ti and the Pd atoms possessed a magnetic moment. As mentioned previously, the bulk magnetization measurements did in fact reveal a residual magnetization, which was field dependent. Indeed, a detailed analysis of Arrott plots has been given elsewhere [6], where it has been demonstrated that the general form shown in figure 5 is quite consistent with this conjecture.

5. Conclusion

The powder neutron diffraction data have established a first-order structural phase transition in Pd_2TiIn. The results do not show the existence of any long-range antiferromagnetic order associated with a large atomic moment as indicated by the static susceptibility data. The results are consistent with an instability of the local moment, which would give rise to the structural phase transition. A more detailed analysis of the magnetic measurements suggest that the ground state is probably ferrimagnetically ordered, which would produce only a small magnetic contribution to the intense nuclear Bragg peaks. Work in progress has revealed that Pd_2TiAl orders magnetically with a spontaneous moment of $\sim 0.2\mu_B$ per formula unit. If this is taken as an indication of the size of the ground state moment in these systems it would be very difficult to determine the magnetic scattering from powder

diffraction data. In order to resolve this problem, single-crystal measurements are required, particularly a polarized neutron diffraction study of the ground state.

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