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Abstract. The ferromagnetic state of CePdSb below 17 K has been confirmed by zero-field Sb NMR. The effective field (B_{eff}) at the Sb nucleus at low temperature is +2.78 T and the quadrupole interaction (ν_q) is 3.8 (2.3) MHz for ^{121}Sb (^{123}Sb). The NMR spectra do not reflect reported magnetic behaviour at 6 K. The transition at this temperature is therefore thought to be due to a second phase. The value of $\partial \ln B_{eff}/\partial P$ is +6.3 Mbar^{-1}, which is similar to that of $\partial \ln T_c/\partial P$, +14 Mbar^{-1}. The value of $\partial \ln \nu_q/\partial P$ is −28 Mbar^{-1}, which is estimated to be ≈ −28 times the value expected for an isotropic elastic solid. The elastic properties of CePdSb are therefore predicted to be extremely anisotropic. The temperature dependence of B_{eff} was measured from 1.4–15 K but measurements are required to lower temperatures before it can be decided whether a 4.5 K gap exists in the spin-wave spectrum, as postulated from heat capacity measurements.

1. Introduction

The compound CePdSb is a ferromagnet whose Curie point ($T_c \approx 17$ K) is remarkably high compared to that of the isostructural Gd compound ($T_N \approx 15.5$ K). The resistivity of CePdSb was found [1] to show a shallow maximum near 150 K, which would suggest that it may be one of a small group of compounds that exhibit both condensed Kondo behaviour and ferromagnetism. The relatively large low-temperature moment, ≈$1\mu_B$/Ce and the low value [2] of the Sommerfeld coefficient, $\gamma = 11$ mJ mol^{-1} K^{-2}, however, rather count against a Kondo state. Three puzzling results have been reported for CePdSb:

(i) the magnetic heat capacity has no peak at T_c;
(ii) a broad maximum is, however, observed at $T_c/2$;
(iii) the low-field magnetization of some samples shows a second transition near $T_c/3$.

In view of these features of the macroscopic properties of CePdSb, a zero-field NMR investigation has been made of the ferromagnetic state as a function of temperature and pressure. A brief report of the NMR spectrum at 4.2 K and atmospheric pressure has already been published [3].

The crystal structure of CePdSb was originally [1] thought to be of the hexagonal CaIn$_2$-type (space group $P6_3/mmc$) with Ce atoms occupying 2b crystallographic sites
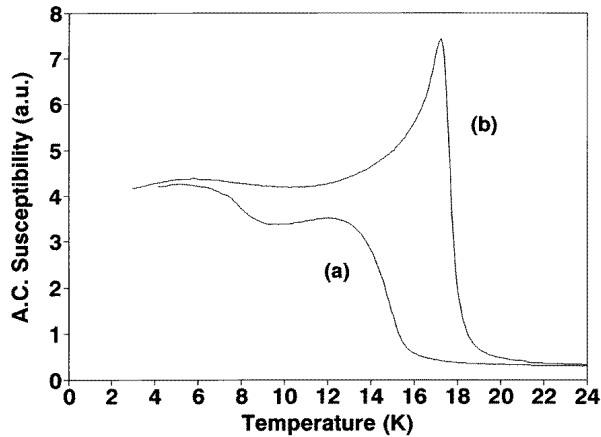
Figure 1. The a.c. susceptibility of polycrystalline CePdSb samples produced (a) in an argon arc furnace (sample II), and (b) in a sealed tantalum capsule at 1800 °C (sample I).
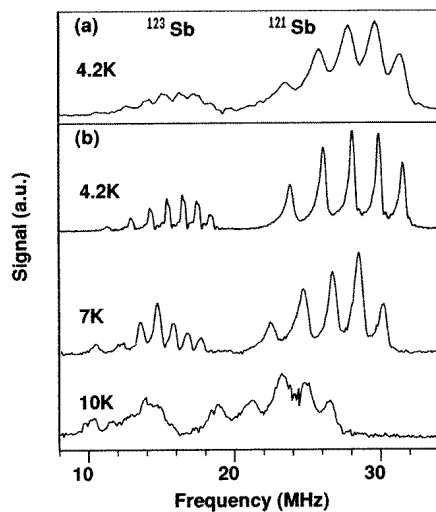
Figure 2. The Sb NMR in CePdSb at various temperatures, prepared (a) in an argon arc furnace (sample II), and (b) as pieces of single crystal grown by the Bridgman method. The single-crystal NMR spectra are similar to those obtained from the polycrystalline powder prepared in a sealed tantalum capsule at 1800 °C.
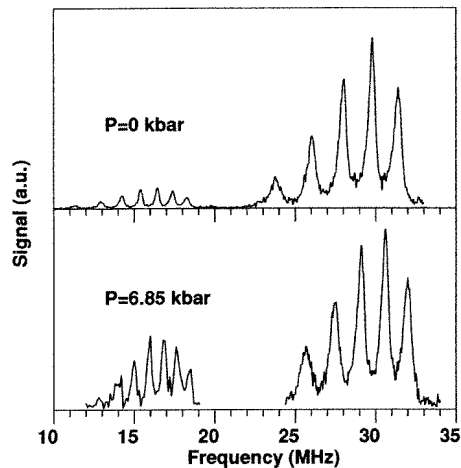
Figure 3. The Sb NMR spectra from CePdSb at atmospheric pressure and 6.8 kbar at 4.2 K for a sample of small single crystals.

and with the Pd and Sb atoms randomly distributed on the 4f sites. Neutron diffraction measurements [3, 4, 5], however, suggested that the crystal structure is a modification of the $CaIn_2$ structure, hexagonal $P6_3mc$ GaGeLi, in which the Pd and Sb atoms form ordered sublattices at coordinates (1/3, 2/3, u) and (2/3, 1/3, v). Profile refinements yield values of $u = 0.4684$ and $v = 0.5164$. The narrow lines observed for the Sb NMR spectrum shown in figure 2 support the suggestion that an ordered crystal structure is formed. The lattice

parameters are $a = 4.935$ Å and $c = 7.890$ Å.

The values of the crystal-field parameters obtained from the inelastic neutron scattering spectra [4] of CePdSb are: $B_2^0 = 1.3$ meV, $B_4^0 = -0.054$ meV and $B_4^3 = 0.857$ meV. These parameters lead to a predicted value of the magnetic moment of $1.2\mu_B$/Ce atom, with the moment lying in the a–b plane [3, 4]. Experimental values for the saturation moment per Ce atom of polycrystalline CePdSb at 4.2 K of $1.2\mu_B$ [1] and $0.95\mu_B$ have been obtained [2]. The low-field magnetization and the a.c. susceptibility as a function of temperature of CePdSb have been reported [2] to show a second maximum near 6 K. It was not clear whether this was due to a magnetic interaction, such as a rotation of the easy axis, or to a second phase.

The magnetic heat capacity (C_M) of CePdSb does not show the usual peak near T_c; rather, C_M gradually increases, with decreasing temperature, to a broad maximum [2] near 9 K, i.e. near $T/T_c = 0.5$. Below 8 K, Trovarelli *et al* [2] found that their data could be well described by the expression $C_M = AT^n \exp(-\delta/T)$, with $A = 0.23$ J mol^{-1} K^{-1}, $n = 1.7$ and $\delta = 4.5$ K. This expression, with $n = 1.5$, is of the form of the spin-wave heat capacity for an anisotropic ferromagnet with a gap δ in the dispersion curve. The magnitude of the gap is however larger than would be expected for an easy-plane ferromagnet. Well above the peak in C_M ($T > 14$ K), C_M is proportional to T^{-2}.

Trovarelli *et al* [2] have proposed two possible explanations for the shape of C_M, both of which, they recognized, are not in complete agreement with the experimental results. Firstly, they note that the Ce–Ce spacing in the CaIn$_2$-type structure is much smaller in the c-direction than in the a-direction and therefore CePdSb might show some features of a low-dimensional system. The T^{-2}-dependence of C_M above 14 K is in agreement with calculations for a magnetic chain, but the fit to the low-temperature side of the peak of C_M is characteristic of an anisotropic three-dimensional ferromagnet. It is therefore necessary to propose that there is a crossover to 3d interactions between 14 K and 8 K. Secondly, they consider a system with incommensurate magnetic order. This is known to exist in GdCu$_5$, due to competition between nearest-neighbour ferromagnetic and next-nearest-neighbour antiferromagnetic interactions. The maximum value of C_M of GdCu$_5$ is far below the Néel temperature, $T_N = 26$ K, but the reason for this is not clear.

In the present paper, we report zero-field NMR experiments on CePdSb, using the ^{121}Sb and ^{123}Sb nuclei, over the temperature range 3 K–15 K and at pressures up to 7 kbar. Two samples were characterized by measuring the a.c. susceptibility as a function of temperature, as shown in figure 1. One was found to show a second maximum in the region of 6 K, but the NMR spectra of the two samples were quite similar at all temperatures. The 6 K transition is therefore attributed to the presence of a second phase. At atmospheric pressure, the temperature dependence of the ^{121}Sb NMR was followed to 15 K (0.88T_c). The accuracy with which the frequency of the resonance could be determined was lower for temperatures greater than 10 K, because of the collapse of the individual quadrupole-split satellite lines into a broad peak. The effective field at the Sb nucleus was found to increase with pressure, with $\partial \ln B_{eff}/\partial P = 6.3$ Mbar^{-1}. The pressure dependence of the electric field gradient at the Sb nucleus was found to be some 28 times greater in magnitude and of opposite sign to that expected from that of a model point charge in an elastically isotropic medium. The elastic properties of CePdSb are therefore likely to be highly anisotropic.

2. Experiment

Two polycrystalline samples of CePdSb and some small pieces of a single crystal were studied via NMR and a.c. susceptibility. Sample I of polycrystalline material was prepared

in a BN crucible contained in a Ta capsule. The capsule was sealed shut by arc welding in an argon atmosphere, in order to avoid loss of Sb when the temperature was raised to 1800 °C. Sample II was prepared in an argon arc furnace. Differences between the two samples may be due to a small loss of Sb during melting in the arc furnace. A 12 g crystal of CePdSb was grown by the Bridgman method. A sealed capsule of the form described for the polycrystalline sample was heated to 1800 °C in an induction coil and then cooled from the bottom end by lowering it slowly through the coil.

The a.c. susceptibility as a function of temperature of the two polycrystalline samples of CePdSb is shown in figure 1. Sample II, prepared by arc melting, clearly shows the peak at 6 K reported previously, but at this temperature there was only a very broad maximum for the sample prepared in a sealed crucible (sample I). It is likely, therefore that the peak in the a.c. susceptibility at 6 K is characteristic of material deficient in Sb; the Curie point of CePd for example [6] is 6.5 K. The response of the unoriented pieces of single crystal was almost identical to that of sample I. (The *c*-axis of CePdSb is known to be the hard direction but it is not necessary to orientate the crystal in order to perform zero-external-field NMR.)

There is no suitable isotope of Ce for NMR but, in the ordered magnetic state, there is a transferred hyperfine field at the Sb nucleus. The ^{121}Sb ($\gamma/2\pi = 10.19$ MHz T^{-1}, $I = 5/2$) and ^{123}Sb ($\gamma/2\pi = 5.52$ MHz T^{-1}, $I = 7/2$) NMR spectra of CePdSb were observed in zero external field. The two nuclei have a natural abundance of ^{121}Sb at 57.25% and ^{123}Sb at 42.75%. The sensitivity (relative to ^{1}H) for equal numbers of nuclei at constant field is 0.160 and 0.0457 respectively. The spectra were measured using a swept frequency phase-coherent spin-echo spectrometer [7, 8], with the sample in a low-Q, untuned coil. Spin echoes were observed at low applied RF power, due to the enhancement of the RF field by domain wall motion, which confirms the ferromagnetic ground state of CePdSb. The Sb NMR spectra (figure 2) show the $2I$ quadrupole-split lines expected from a site of non-cubic symmetry. The sign of the effective field at the Sb nucleus (B_{eff}) was shown to be positive, i.e. parallel to the magnetization, by observing the increase in the NMR frequency in a field of 0.1 T. The high-pressure experiments were performed in a Be–Cu lock cell. The pressure was applied to the liquid immersed sample at room temperature. The pressure was measured using a calibrated semiconductor transducer.

The NMR spectra shown in figures 2 and 3 are taken from the sample consisting of pieces of single crystal. Although the signal was weaker in the sample of small single crystals than for the powder sample I (because of RF skin depth) the lines were better resolved. The line positions of the sample of small single crystals appeared at almost identical frequencies to those observed for sample I. As can be seen from figure 2, sample II gave similar spectra, but with broader lines. The broader lines of sample II may be a signature of the loss of the Sb. A disordered occupation of Sb sites may result in local distortion of the electric field gradient, leading to inhomogeneous quadrupole broadening. The detailed analysis of the behaviour of CePdSb, described below, is therefore based on our measurements on the sample consisting of single crystals.

3. Discussion

The low-temperature ^{121}Sb and ^{123}Sb NMR spectra of CePdSb show $2I$ quadrupole-split lines; see figure 2. In order to analyse the spectrum it is necessary to go to second order in the expression for the frequencies because ν_Q/ν_0 was found to be 0.135 (0.15) for ^{121}Sb (^{123}Sb). Because CePdSb is an *a–b* easy-plane magnet we can take the magnetic moment in the ordered state to be at 90° to the electric field gradient (EFG) and fit the

spectra to the equation [9]

$$\nu(m \leftrightarrow m-1) = \nu_0 - \frac{\nu_Q(2m-1)}{4} - \frac{\nu_Q^2}{32\nu_0}[6m(m-1) - 2I(I+1) + 3].$$

Here, $\nu_0 = 2\pi B_{eff}/\gamma_n$ and $\nu_Q = 3e^2qQ/2hI(I-1)$, where eQ is the quadrupole moment of the nucleus and eq the EFG at the nucleus. Separate fits were made to ^{121}Sb and ^{123}Sb spectra and at 4.2 K at atmospheric pressure the values of ν_0 are 27.77 MHz and 15.05 respectively, and ν_Q are 3.80 and 2.27 respectively. The ratio of ^{121}Sb/^{123}Sb for $\nu_0(\nu_Q)$ is therefore 1.845(1.67), in excellent agreement with published values [10] for the NMR of Sb of 1.847(1.65), confirming the validity of the fit. The sign of B_{eff} was found to be positive, i.e. parallel to the magnetization, because ν_0 increased when a field of 0.1 T was applied.
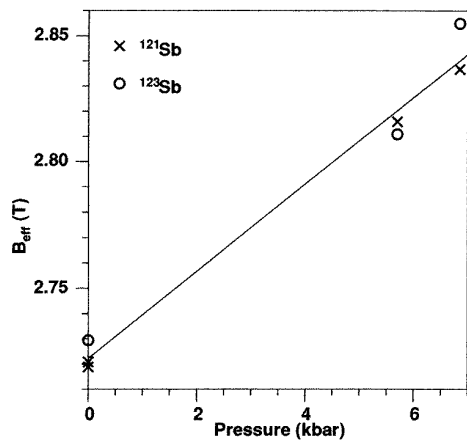
Figure 4. The pressure dependence of B_{eff} at the Sb nucleus at 4.2 K for a sample of small single crystals of CePdSb.
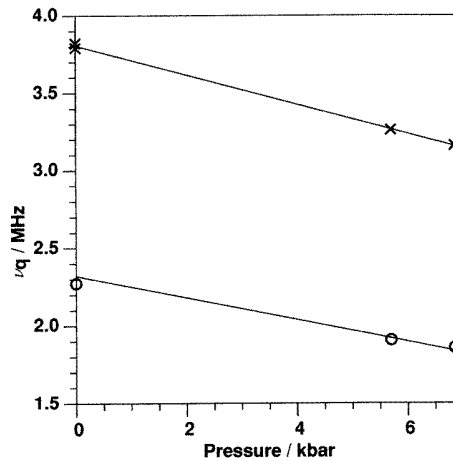
Figure 5. The pressure dependence of ν_Q at 4.2 K for the single-crystals sample of CePdSb.

The NMR spectra at atmospheric pressure and 6.85 kbar at a temperature of 4.2 K are shown in figure 3. It is clear that ν_0 increases and ν_Q decreases under pressure. The value of B_{eff} was found to increase linearly under pressure, figure 4, with $\partial \ln B_{eff}/\partial P = +6.3$ Mbar^{-1}. This value is comparable to the pressure dependence of the Curie point, $\partial \ln T_c/\partial P = 14$ Mbar^{-1}. The effective field at the Sb nucleus probably arises from a RKKY-like polarization of the conduction electrons by the Ce moments. In the RKKY model, the interaction is a function of $\mathbf{k}_F \cdot \mathbf{r}$, where $\mathbf{k}_F$ is the Fermi wave vector and in a nearly free-electron model $\mathbf{k}_F \cdot \mathbf{r}$ is independent of pressure. The change of B_{eff} with pressure could therefore arise from an increase in the Ce moment or of the exchange interaction with pressure. The pressure dependence of the magnetization of CePdSb has not been reported, but the value of $\partial \mu/\partial P$, where μ is the Ce moment, is expected to be small. The value for CePt is 0 ± 1 Mbar^{-1}, for example [11].

The pressure dependence of ν_Q is shown in figure 5. The value of $\partial \ln \nu_Q/\partial P = -28$ Mbar^{-1}. The elastic properties of CePdSb have not been reported, but the bulk modulus B_T of a number of Ce intermetallic compounds lies in the range [12] 0.8–1.2 Mbar. Taking 1 Mbar as a reasonable estimate of the bulk modulus therefore leads to a value of $\partial \ln \nu_Q/\partial \ln V = 28$. The theoretical value of $\partial \ln \nu_Q/\partial \ln V$ for an elastically anisotropic solid is -1 and, while this model is too simple for a real solid, values close to -1, e.g. -1.5

for Cu in Cu_2O, have been measured [13, 14]. The value of $\partial \ln \nu_Q/\partial \ln V$ for CePdSb is therefore some 28 times greater, and of opposite sign, to that for the simple model. Because, from the values of B_{eff}, there is no suggestion that the magnetic properties of CePdSb change drastically under pressure, it is unlikely that the large value of $\partial \ln \nu_Q/\partial \ln V$ relates to a change in the electronic structure of the Ce ion. The most probable explanation is that the elastic properties of CePdSb are like those of compounds such as CuO [13], in that they are extremely anisotropic, and so the relation $\partial \ln \nu_Q/\partial \ln V = -B_T \partial \ln \nu_Q/\partial \ln P$ is not valid.

The spontaneous magnetization of CePdSb as a function of temperature, derived by extrapolating the magnetization to zero external field in an Arrott plot [5], shows a point of inflexion near 10 K, and then a rather slow approach to the region of the Curie point (17 K). Because the magnetic heat capacity C_M is proportional to $\mathrm{d}M^2/\mathrm{d}T$, the magnetization data are consistent with the 10 K peak observed in C_M. The Arrott plots are not, however, linear, so the accuracy of the extrapolation of the magnetization to zero field is difficult to estimate. Sb NMR spectra of the single-crystal and powder samples were measured as a function of temperature at atmospheric pressure in zero applied field.
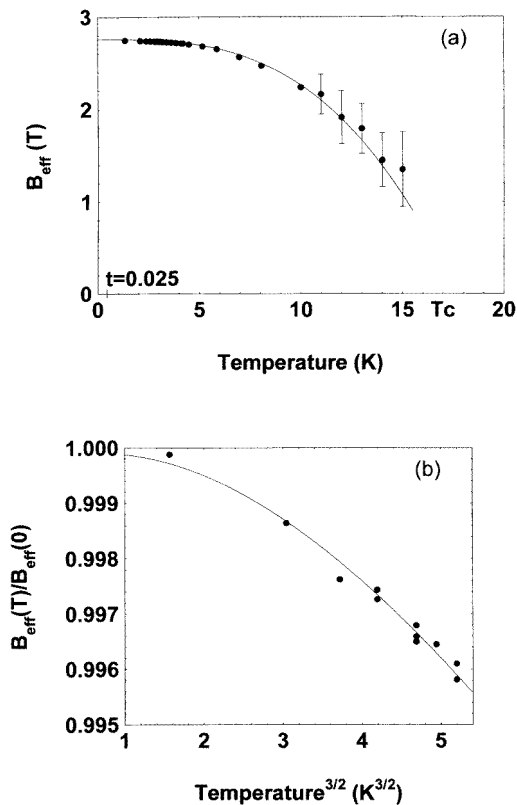
Figure 6. (a) The temperature dependence of B_{eff} at the Sb nucleus in CePdSb at atmospheric pressure. The collapse of the satellite lines above 10 K reduces the accuracy with which B_{eff} can be determined. The line has a t^3-dependence. True $t^{3/2}$-behaviour may not appear above $t = 0.025$. (b) The variation of $B_{eff}(T)/B_{eff}(0)$ with $T^{3/2}$ in the low-temperature region. The line is the model fit including the gap function.

The lowest attainable temperature was 1.35 K, and the highest useful temperature was constrained by the collapse of the quadrupole-split NMR spectrum into a single broad distribution as shown in figure 2. The temperature dependence of B_{eff}, shown in figure 6(a), shows a slower decrease with temperature than the decrease in spontaneous magnetization [5], with no indication of the point of inflexion around 10 K. The assumption is made that the effective field at the nucleus is proportional to the spontaneous magnetization in the low-temperature limit. The validity of this assumption is discussed in [15, 16, 17]. On this assumption, the decrease of the magnetization of an isotropic ferromagnet with temperature is given by spin-wave theory:

$$M_T/M_0 = B_{eff}(T)/B_{eff}(0) = 1 - bt^{3/2} \tag{1}$$

where $t = T/T_c$, $b = 2.612(g\mu_B/M_0)(k/4\pi D)^{3/2}$, g is the Landé factor, k is the Boltzmann constant, and D is the spin-wave stiffness. Anisotropy leads to a gap in the spin-wave spectrum, $T_g = g\mu_B B_A/k_B$, and equation (1) is modified by $f(T/T_g)$ as discussed by Keffer [15] for example.

Above the low-temperature limit, terms in $t^{5/2}$ and $t^{7/2}$ appear and, in general, it is necessary to integrate over the Brillouin zone to find $M(T)/M(0)$. Indeed in the range $0.17 < t < 0.6$, B_{eff} appears to vary as t^3, showing the importance of the higher-order terms. The region for which equation (1) applies is rather limited. For Ni and Fe for example [17, 16], it is $t < 0.025$. The low-temperature Curie point of CePdSb made it impossible for us to reach $t < 0.075$ so the measurements shown in figure 6 may not be in the low-temperature limit. Without making these very low-temperature measurements, it is not possible for us to determine $B_{eff}(0)$ unambiguously, or to decide whether the curvature seen in figure 6(b) is due to a gap in the spin-wave spectrum or the presence of terms beyond $t^{3/2}$.

The data can, however, be fitted consistently across the range $0.075 < t < 0.17$ by the function [15]

$$B_{eff}(T)/B_{eff}(0) = 1 - (b/2.612)t^{3/2} \sum_{p=1}^{\infty} p^{-3/2} \exp(-pT_g/T)$$

i.e. equation (1) modified by the presence of a gap in the spin-wave spectrum. Taking $g = 18/7$ (the value of g parallel to the a–b plane as derived by Trovarelli *et al* [2]), the moment per Ce atom as $1.2\mu_B$ and $D = 11$ meV after Neville *et al* [5], we obtain a value of $T_g = 4.0$ K, close to the value $T_g = 4.5$ K found from heat capacity measurements [2].

4. Conclusions

The ferromagnetism of CePdSb has been investigated as a function of temperature and pressure using zero-field Sb NMR. The second magnetic transition near 6 K, which was reported earlier, was found in the a.c. susceptibility of one of the two samples studied. Because the NMR spectra of the two samples were very similar, this transition is considered to be due to a second phase, rather than to be an intrinsic feature of CePdSb. The temperature dependence of the Sb NMR of CePdSb appears to be that of a normal ferromagnetic material, despite the peculiar behaviour of the magnetic heat capacity. The effective magnetic field at the Sb nucleus increases under pressure at a rate comparable to that of the Curie point. The pressure dependence of the electric field gradient at the nucleus is, however, some 28 times greater than, and of opposite sign to, that expected from a simple point charge model of elastic isotropy. The temperature dependence cannot be fully understood in terms of spin-wave theory without making measurements below 1 K, and to complete the analysis

of the properties of CePdSb under pressure, a measurement of the elastic properties and pressure dependence of the magnetization is required.

Acknowledgments

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