Thermal expansion of CePdSb near the ferromagnetic transition

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The thermal expansion of CePdSb has been measured between 1.6 and 30 K in magnetic fields of up to 8 T. The magnetic contribution to the linear thermal-expansion coefficient of polycrystalline CePdSb (α_p) in zero magnetic field has a maximum value near 10 K and becomes small by 20 K. There is no peak in α_p at the Curie point, $T_C = 17$ K. This anomalous behavior is in agreement with earlier heat-capacity measurements. The maximum value of α_p decreases in a magnetic field and moves to a higher temperature. The thermal expansion of a single crystal of CePdSb was found to be highly anisotropic. In the magnetically hard c direction the thermal-expansion coefficient (α_c) has a maximum value near 10 K some three times larger than that of the peak in α_p. The value of α_c is negative above T_C and then shows the beginnings of a normal critical response near T_C before being submerged in the broad 10 K peak. The values of α_a (α_b) are small in magnitude and negative (positive) below 14 K in zero field but both become positive in a field of 8 T. The strong secondary peak in the ac susceptibility of CePdSb reported earlier, some 11 K below T_C, was observed in samples prepared by arc melting but not in those produced in sealed crucibles and is therefore probably due to material with a deficiency of Sb. [S0163-1829(96)01630-X]

I. INTRODUCTION

Magnetization,[1] NMR,[2] and neutron diffraction[2–4] measurements show that CePdSb is a ferromagnet with a Curie point (T_C) near 17 K. The behavior of the magnetic heat capacity (C_M) however has been reported[5] to be anomalous. The magnitude of C_M begins to increase below 25 K, and reaches a maximum value near 10 K, but shows no feature at T_C. A second curious property of CePdSb is a secondary maximum in the ac susceptibility and low-field magnetization[5] some 11 K below T_C. Since CePdSb is also unusual in that its magnetic transition temperature is higher[1] than that of GdPdSb ($T_N \cong 15$ K), it shows a Kondo-like maximum in the resistivity[1] near 150 K, and there are puzzling features of the inelastic neutron and μSR experiments, we have performed thermal-expansion measurements on polycrystalline and single-crystal samples of CePdSb in fields of up to 8 T.

The crystal structure of CePdSb is hexagonal[1] with $a = 4.5935$ Å and $c = 7.890$ Å. Neutron powder-diffraction measurements are consistent with either the $CaIn_2$ structure ($P6_3/mmc$), in which the Pd and Sb are randomly distributed on the f sites, or the GaGeLi ($P6_3mc$) structure, where the Pd and Sb are ordered. From measurements of crystal-field splittings on a number of CeTX compounds however it was possible to conclude[2,3] that CePdSb has the ordered GaGeLi structure.

The saturation moment per Ce atom of CePdSb has been estimated[1,5] from magnetization measurements on polycrystalline material to be 1.2 or $0.95\mu_B$. Neutron-diffraction measurements lead to a moment of $1.2\mu_B$ lying in the basal plane. Low-field (1 G) magnetization[3] measurements on a single crystal show a slightly larger magnetic response along the b axis than along a, and the thermal expansion below T_C will be seen below to be quite different for a and b. Inelastic neutron-scattering measurements at high temperature suggest that only nearest-neighbor Ce-Ce exchange is important.[4] This localized model may explain why dT_C/dP is positive,[1] which is unusual for a metallic ferromagnet with a low Curie point.

In the present paper we report the results of measurements of ac susceptibility (χ_{ac}) and thermal-expansion measurements on polycrystalline and single-crystal specimens of CePdSb. The low-temperature peak in χ_{ac} is not found for material prepared in a sealed crucible and is therefore attributed to samples deficient in Sb. The temperature dependence of the thermal-expansion coefficient of the polycrystalline material (α_p) confirms the results of the heat-capacity measurements: there is no peak at T_C but only a broad maximum near 10 K. In a magnetic field, the value of the maximum is reduced and the peak moves to higher temperature. The single-crystal measurements show that the 10 K peak arises almost entirely from the thermal expansion of the c axis. Furthermore, the thermal-expansion coefficient in the c direction (α_c) does show the beginnings of a critical peak, but this is then absorbed into the broad 10 K maximum. Below 14 K the value of α_a (α_b) is small in magnitude and negative (positive). In a field of 8 T it becomes positive for both a and b.

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II. EXPERIMENTS

The thermal-expansion measurements were made in a parallel-plate capacitance cell that had been calibrated using the known thermal expansivity of copper and sapphire. A magnetic field of up to 8 T could be applied parallel to the measured direction. The lowest temperature attainable in the variable temperature insert was 1.6 K. The ac susceptibility as a function of temperature was measured in an uncalibrated mutual-inductance apparatus.

Two polycrystalline samples of CePdSb and two pieces of a single crystal were investigated. Sample I of the 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, and the differences between the two samples may be due to a small loss of Sb during melting.

A 12 g crystal of CePdSb was grown using the Bridgeman method. A sealed capsule of the form described for the polycrystalline sample I was heated to 1800 °C in an induction coil and then cooled from the bottom end by lowering it slowly through the coil. The measurements were made on rods or discs prepared by spark machining.

In order to find the magnetic contribution to the thermal expansion of CePdSb it is necessary to measure that of a nonmagnetic analog. The natural choice would seem to be LaPdSb but, as has already been reported,[5] this material does not follow the expected $\gamma T+\beta T^3$ behavior below 4.5 K. We have therefore chosen the same reference material, LaAgGe, as was used by Trovarelli *et al.* to correct their specific-heat data. It will be seen below, however, that the correction is small at temperatures below the Curie point.

III. EXPERIMENTAL RESULTS

The samples of CePdSb were characterized by measuring χ_{ac} as a function of temperature (Fig. 1). Sample I of the polycrystalline material showed a sharp ferromagnetic transition near 17.5 K, in agreement with earlier measurements, but did not show the large peak at 6 K reported[5] by Trovarelli *et al.* However, their sample was prepared by arc melting and our sample II, prepared by the same technique, shows an even larger peak at 6 K and a lower transition temperature than sample I. The peak at 6 K in sample II probably arises from a deficiency of Sb in samples prepared without encapsulation. The Sb NMR linewidth observed[2] for sample I in the ferromagnetic state was narrower than for sample II, which supports the view that there is more randomness of composition in the latter. A second possibility is that sample I tends to favor the GaGeLi structure, with ordered Sb and Pd sites, while sample II is closer to the random arrangement of Sb and Pd found in the $CaIn_2$ structure.

The *c* axis of the single crystal is seen in Fig. 1 to be the hard direction. The *a* and *b* directions had almost identical responses. Static low-field measurements ($B=1$ G) on a small piece of the same crystal[3] have also indicated that *c* is the hard axis, and show a slightly larger peak at about 10 K for the *b* axis than that for the *a* axis. The thermal-expansion measurements described below make it clear that the *a* and *b* axes are not identical in the ferromagnetic region. The shape of the χ_{ac} response as a function of temperature for the *a* and *b* axes is in good agreement with that of sample I of the polycrystalline material.

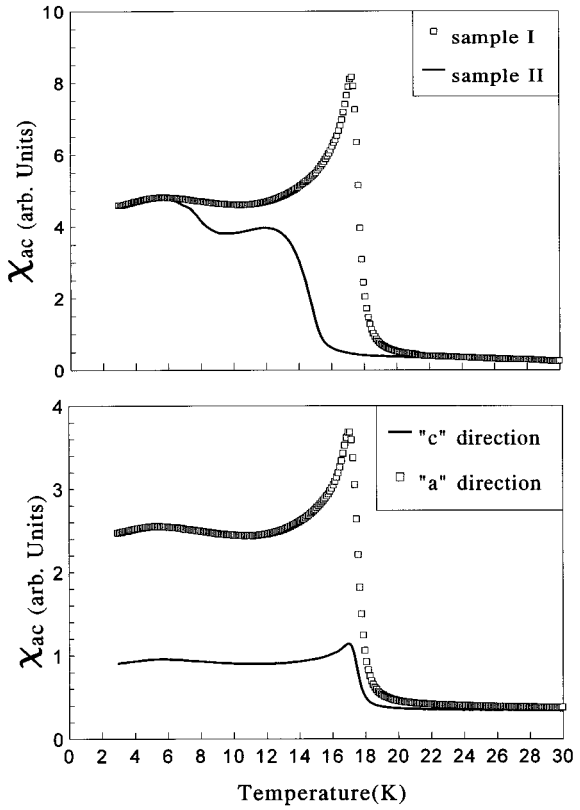

FIG. 1. The upper graph shows the ac susceptibility as a function of temperature for two polycrystalline samples of CePdSb, see text, and the lower graph for two directions in a single crystal. The *b*-axis response was almost identical to that of the *a* axis.

The coefficient of thermal expansion of polycrystalline CePdSb in the temperature range below 30 K is shown in Fig. 2. In zero field there are differences of detail between samples I and II but the general appearance is the same and is also in agreement with the heat-capacity measurements. In all three cases there is no trace of the ferromagnetic transition near 17 K but only a broad peak with a maximum near 10 K. The maximum value of α_p, and the temperature at which it occurs, differ for samples I and II but the values of the integral of α_p/T, which is proportional to the magnetic entropy for a constant Grüneisen factor, agree within 15%.

The application of an 8 T magnetic field, parallel to the measurement direction, reduces the maximum value of α_p, and increases the temperature at which it occurs by some 3.5 K for sample I and 3.1 K for sample II. Since the single-crystal thermal expansion is very anisotropic, the differences between samples I and II may be partly due to a different distribution of crystallites as well as to a deficiency of Sb in sample II.

The single-crystal data are shown in Fig. 3. It is clear that the peak of α_p at 10 K in zero magnetic field arises almost entirely from the thermal expansion along the *c* axis. The other new result from the measurements on a single crystal of CePdSb is that there is the beginning of a normal critical behavior in α_c near T_C but that it is concealed by the broad 10 K peak. The sign of α_c also changes from negative to

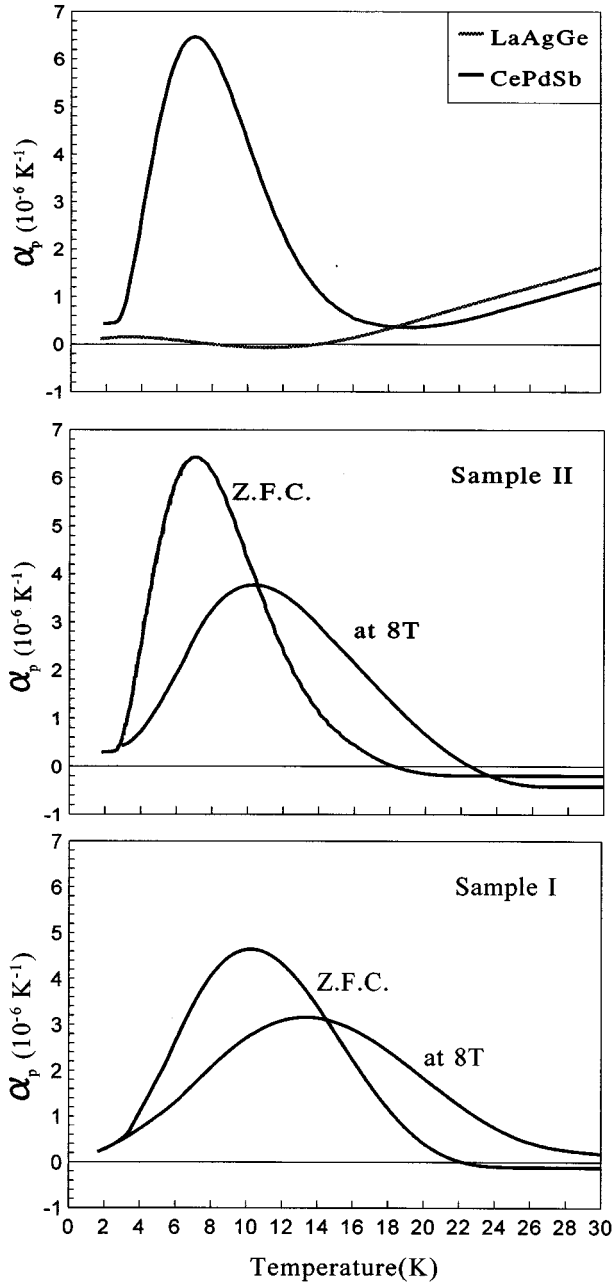

FIG. 2. The linear thermal-expansion coefficient α_p of polycrystalline sample II of CePdSb and of LaAgGe as a function of temperature (top). The magnetic contribution to the linear thermal-expansion coefficient of polycrystalline CePdSb as a function of temperature in zero field and a field of 8 T (center and bottom).

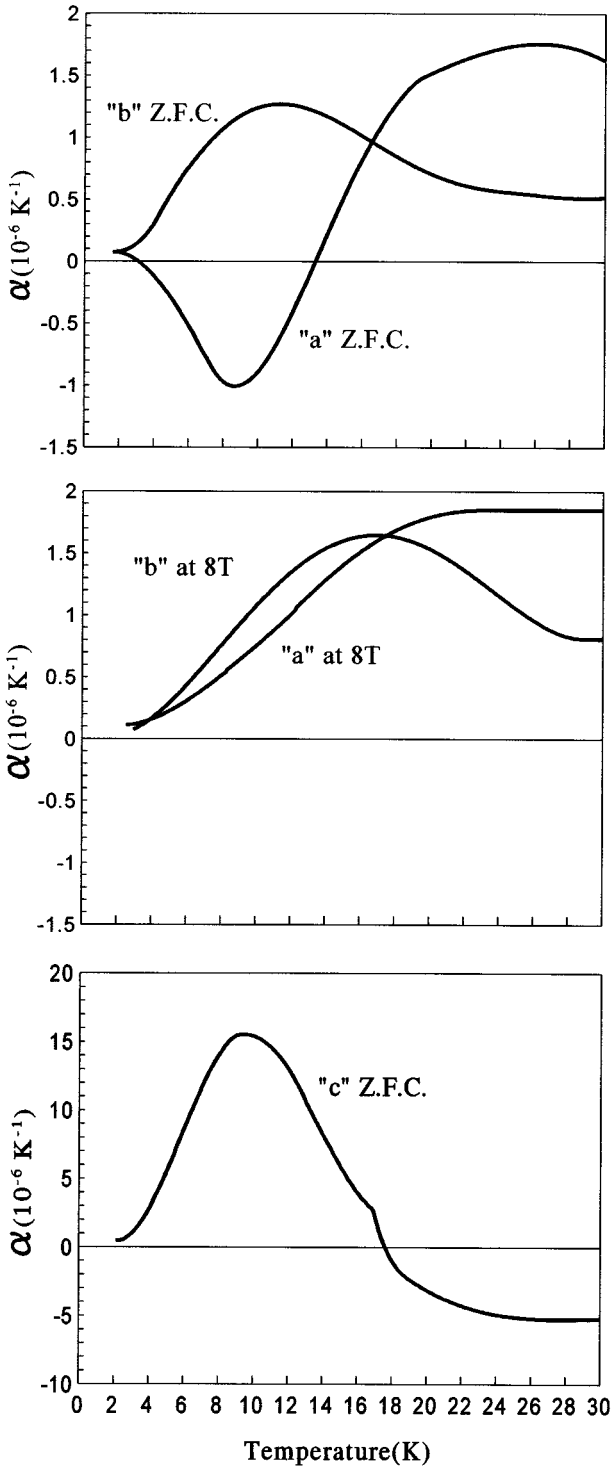

FIG. 3. The linear thermal-expansion coefficient of a single crystal as a function of temperature along the a and b axes of CePdSb in zero field (top) and in a field of 8 T (center). That along the c axis in zero field is shown at the bottom.

positive near T_C, i.e., the sample length in the c direction is a maximum near T_C.

The measured values of α_a (α_b) are small in magnitude and negative (positive) below 14 K, so that their sum is close to zero. It should be noted however that α_c is an order of magnitude greater than α_a or α_b, and since there is known to be a mosaic spread in the crystal, there may be an appreciable error in these results. In a field of 8 T both α_a and α_b become positive and of comparable size, as shown in Fig. 3. The parallel magnetostriction at 2.6 K for the a and b axes of the single crystal and for polycrystalline material is shown in Fig. 4. The design of the capacitance cell does not allow the application of a magnetic field along the magnetically hard c axis. Apart from a rapid decrease in length L at low field, due to the removal of domain walls, it was found that $\partial \ln L/\partial B$ was independent of B with a value at 2.6 K of $(-2.1, -2.4, -1.7,$ and $-2.0)10^{-6}$ T^{-1} for polycrystalline samples I and II and for the a and b axes of the single crystal, respectively. This suggests that $\partial \ln L/\partial B$ for the c direction is

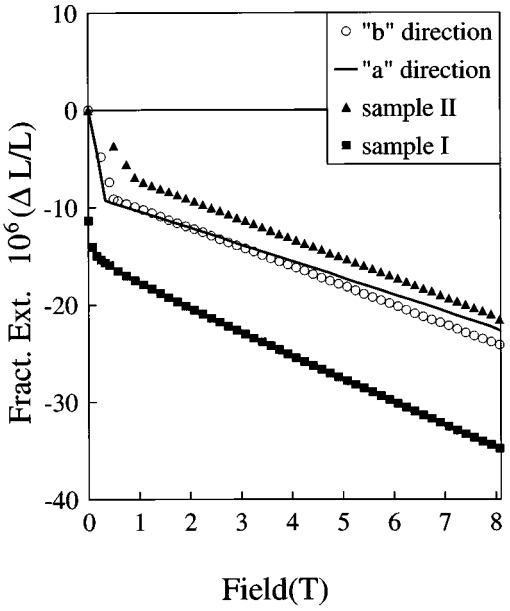

FIG. 4. The parallel magnetostriction of CePdSb for the *a* and *b* directions of a single crystal and polycrystalline samples I (squares) and II (triangles) at 2.6 K.

comparable with that of *a* and *b*.

In summary, the present thermal-expansion measurements on polycrystalline CePdSb are consistent with those of the magnetic heat capacity in not showing any anomaly at T_C, but the single-crystal measurements provide the additional information that only the *c* axis makes a significant contribution to the low-temperature thermal expansion in zero magnetic field.

IV. DISCUSSION

The origin of the unusual thermodynamic behavior of CePdSb below 20 K is still not clear. In this section we summarize the conclusions to be drawn from the experiments carried out so far and suggest some experiments that are required to clarify the problem.

Apart from the 10 K peak in α, the thermal expansion and magnetostriction of CePdSb at low temperature may be understood qualitatively as arising from the contraction (expansion) of the lattice parallel (perpendicular) to the Ce moment. In zero magnetic field the moments turn in to the *a*-*b* plane near T_C and the length in the *c* direction reaches a maximum value. Below 14 K the moment preference[4] for the *b* axis over the *a* axis is seen as the length along *a* goes through a minimum due to the magnetic contribution to α_a having the opposite sign to the normal decrease of length with temperature. A large magnetic field along *a* or *b* aligns the Ce moments and hence the parallel magnetostriction is negative.

The measurements of C_M and α_p below 20 K show essentially the same behavior. The values of α_p for sample I can be scaled to C_M using the conversion factor 1×10^{-6} $K^{-1}\equiv1.3$ J mole^{-1} K^{-1}. A single Grüneisen factor (γ_G) can therefore be calculated for the whole ferromagnetic region. The volume v of one formula unit of CePdSb is 72×10^{-30} m^3, the value of the bulk modulus (B_T) is not known but must be $\approx10^{11}$ Pa, so $\gamma_G=3\alpha_pN_Avb_T/C_M\cong10$, considerably larger than the value ($\cong2$) for simple metals.

Trovarelli *et al.* fitted[5] their values of C_M up to 8 K, i.e., just below the 10 K peak, with an expression of the form,[6] const $T^n\exp(-\delta/T)$ with $n=1.7$ and $\delta=4.5$ K, a three-dimensional (3D) ferromagnet with a gap in the spin-wave spectrum. Above 14 K there was a fit to the form $C_M\sim T^{-2}$. They suggested that, due to the geometry of the CePdSb lattice, there was a low-dimensional character to the magnetization[7] between T_C and 8 K, and then anisotropic 3D magnetism with a gap of 4.5 K in the spin-wave spectrum. Alternatively, they considered the possibility that CePdSb could be a frustrated ferromagnet,[8] but this would not explain the lack of a peak in C_M at T_C.

Due to the crystal field, the ground state of Ce in CePdSb is a doublet separated by more than 200 K from the first excited state. The susceptibility data have been analyzed[5] in terms of an effective spin 1/2 with $g_\parallel=6/7$ and $g_\perp=18/7$, relative to the *c* axis. The T^{-2} behavior of C_M and α above the 10 K peak is consistent with a Schottky anomaly of a two-level system, so it is worth considering the extent to which the behavior over the whole temperature range below 30 K could be described by the Schottky heat-capacity equation. The peak in the heat capacity of a two-level system with energy gap Δ occurs at a temperature T_M such that $\Delta=2.4k_BT_M$. The application of an external field B_0 to the two-level system would lead to $\Delta+g\mu_BB_0=2.4k_BT'_M$. The heat capacity has not been measured in a magnetic field, but it was seen above that C_M in zero field is proportional to α_p, so we use the change in the temperature of the peak value of α_p and α_b in a field of 8 T to define an effective *g* factor for CePdSb.

The value of (T'_M-T_M) for the *b* axis of the single crystal in a field of 8 T is 5.7 K, see Fig. 3, leading to a value for *g* of 2.55 in excellent agreement with the value of $g_\perp$, 18/7 $=2.57$, found from the susceptibility measurements. The effective *g* values for the polycrystalline samples are 1.56 and 1.38 for I and II, respectively. The value of $(g_\parallel+2g_\perp)/3$ is 1.43. The change in the position of the temperature of the peak of the thermal expansion of CePdSb in a magnetic field is therefore consistent with the increase in the energy gap of a two-level system.

Attempts to fit the values of C_M, α_b, or α_p for the whole temperature range below 30 K to a Schottky anomaly are, however, not successful. The peak value of C_M is not correct and, if Δ is taken as a constant, the coefficient of the T^{-2} term is too large. Conversely, if Δ is treated as arising from a molecular field and scaled with the magnetization, then the values of C_M above the 10 K peak are too small.

The present single-crystal thermal-expansion measurements support the view that 10 K represents some kind of boundary temperature for CePdSb. Near 10 K, α_a is a minimum and α_c a maximum. Inelastic-neutron measurements[4] also see a change in behavior near 10 K. At 2 and 6 K a spin-wave dispersion was observed, with spin-wave stiffness $D\approx10-12$ meV. This disappeared at 10 K and was replaced by a diffusive response centred at zero energy transfer. A longitudinal μSR experiment[4] provided further confirmation of the unusual properties of CePdSb. In a normal polycrystalline ferromagnet the asymmetry becomes negligible below T_C, because of the random distribution of internal fields, but in CePdSb at 10 K, it had only decreased by a factor of 2

from the high-temperature value. Also, the damping rate, once the contribution from the Sb nuclear moments had been suppressed, was found to be constant through the ferromagnetic transition.

While all the above experiments support the view that something changes in the character of the magnetization of CePdSb near 10 K, it is clear from Fig. 1 that it does not affect the ac susceptibility, whose behavior is that of a conventional ferromagnet. The temperature dependence of the spontaneous magnetization does however show[4] a change of slope near 10 K and a very slow approach to T_C. Since $C_M \sim dM^2/dT$, the peak in C_M is consistent with the spontaneous-magnetization measurements.

The first priority for further measurements is to confirm or disprove the existence of the 4.5 K gap in the spin-wave spectrum below 8 K which provides a satisfactory fit to C_M. This could be determined either by better resolution in the inelastic neutron-scattering experiments or by measurements of spontaneous magnetization or zero-field Sb NMR at temperatures well below 1 K. A second problem is the nature of the magnetization in the basal plane. Crystal-field theory alone would make the a and b axes identical, but it is clear from the thermal-expansion measurements that the magnetoelastic interaction is different for a and b. Finally, the problem remains to explain the large $(R/2)\ \ln 2$ change of entropy of CePdSb between 0 and 10 K, since the ground state is a doublet split by the exchange field.

V. CONCLUSION

Thermal-expansion measurements on polycrystalline CePdSb agree with magnetic heat-capacity results: in zero external field there is no peak at T_C ($\cong$17 K) but a broad maximum near 10 K. In a field of 8 T the value of the maximum decreases and moves to some 14 K. Single-crystal measurements show that the 10 K peak seen in the polycrystalline material is due to the thermal expansion of the c axis. Below 14 K the thermal-expansion coefficient of the $a(b)$ axis is small in magnitude and negative (positive). Further measurements are required to establish if there is a 4.5 K gap in the spin-wave spectrum, as proposed to explain the behavior of C_M at low temperature.

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