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Study of the specific heat of a $CeCoAl_4$ single crystal in high magnetic fields

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Abstract

The specific heat of a $CeCoAl_4$ single crystal has been studied in magnetic fields up to 17.5 T. In zero field, this compound has been found to order antiferromagnetically below the Néel temperature of about 13.5 K. The effect of the magnetic field is different when it is applied along the different crystallographic axes. Along the *a*-axis, with increasing magnetic field, the Néel temperature slightly decreases and reaches a value of 12.7 K at 17.5 T. Along the *b*-axis, the Néel temperature decreases more strongly with increasing magnetic field. At 16 T, we found a value of T_N of about 6.9 K. At 17.5 T, along the *b*-axis, we observed a rather broad peak in the specific heat which is associated with a transition from paramagnetism to ferromagnetic order. Along the *c*-axis, a drastic change in the specific heat occurs at a field between 7–8 T. At 7 T, the value of T_N is about 9 K. At fields higher than 8 T, the specific heat is evidently characterised by a transition from paramagnetism to ferromagnetic order. The critical values of the magnetic field above which ferromagnetic order is formed at low temperature turn out to be consistent with the measurements of the magnetisation curves at 4.2 K. © 1998 Elsevier Science S.A. All rights reserved.

Cerium cobalt aluminide; Antiferromagnetic ordering; Magnetic structure; Crystal field specific heat

1. Introduction

The $CeCoAl_4$ compound crystallises in the orthorhombic $LaCoAl_4$ structure [1]. The Co atoms are non-magnetic and hence the magnetic properties are entirely determined by Ce–Ce interactions, together with the magneto-crystalline anisotropy (MCA). From the magnetic measurements [2,3], it was found that Ce is trivalent. The moments order antiferromagnetically below $T_N = 13.5$ K. The field dependence of the magnetisation at 4.2 K is strongly anisotropic. Along the *c*-axis, the Ce-moments turned out to become parallel via a spin–flop transition at about 7.3 T. Along the *b*-axis, a gradual bending process was observed which is completed above a critical field of 17 T. Along the *a*-axis, up to 20 T, the Ce-moments are still far from being parallel. At the highest field (20 T) measured, the observed (saturation) moment is fairly low in comparison with the free Ce^{3+} value of 2.14 μ_B/Ce at. (i.e. 1.53 μ_B/Ce at. along the *c*-axis and 1.11 μ_B/Ce at. along the *b*-axis). This fact as well as the strong magnetisation anisotropy along the *c*- and the *b*-axes can be taken as an indication that the MCA in $CeCoAl_4$ is relatively strong and plays an important role in determining the magnetic properties. In order to obtain more information on the crystal field splitting in $CeCoAl_4$, we will report on the specific heat of $CeCoAl_4$ in high magnetic fields.

2. Experimental

The $CeCoAl_4$ single crystal was grown by means of a modified tri-arc Czochralski technique. Detailed analyses point to an almost perfect quality of the crystallinity and a composition ratio of 0.98:1:3.91 for Ce:Co:Al. More detailed information on the growth can be found elsewhere [3]. The specific-heat measurements were carried out in the 17.5 T high-field facility at the University of Amsterdam in the temperature range 0.3–90 K [4,5]. The zero-field

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specific measurements were also carried out on another facility which allows measurements from 1.4–300 K [6].

3. Results and discussion

The specific heat of $CeCoAl_4$ and $LaCoAl_4$ measured in zero field is plotted as C/T vs T in Fig. 1. For $CeCoAl_4$, a sharp peak is observed at the ordering temperature T_N of about 13.5 K. Well above T_N, the specific heat curve of $CeCoAl_4$ almost coincides with that of $LaCoAl_4$.

The magnetic contribution to the specific heat of $CeCoAl_4$ is obtained by subtracting the phonon and electronic contribution as derived from $LaCoAl_4$. The magnetic entropy S_m vs T is drawn in the inset of Fig. 1. At 220 K, the magnetic entropy S_m is 14.7 $J\,mol^{-1}K^{-1}$ which is very close to the full value of $R\ln 6 = 14.9$ $J\,mol^{-1}K^{-1}$ as expected for Ce^{3+} with $J=5/2$ (R is the gas constant).

In Fig. 2 we plot the ratio C/T vs T of $CeCoAl_4$ measured in different fields applied along the main axes. Along the a-axis, there is hardly any field effect on the specific heat. In a field of 17.5 T along the a-axis, the value of T_N is 12.7 K to be compared with the value of 13.5 K in zero field. Along the b-axis, below 16 T, we still observe a sharp peak which is characteristic for the transition from paramagnetic to antiferromagnetic order. The peak is shifted towards lower temperatures with increasing magnetic field. At 17.5 T, the peak becomes a shoulder. This field is sufficient to force the Ce moments parallel along the b-axis at 4.2 K [2]. Along the c-axis, in fields between 7 and 8 T at which a spin-flop transition occurs in the magnetisation curve at 4.2 K, the character of the peak changes from a sharp peak to Schottky-like behaviour.

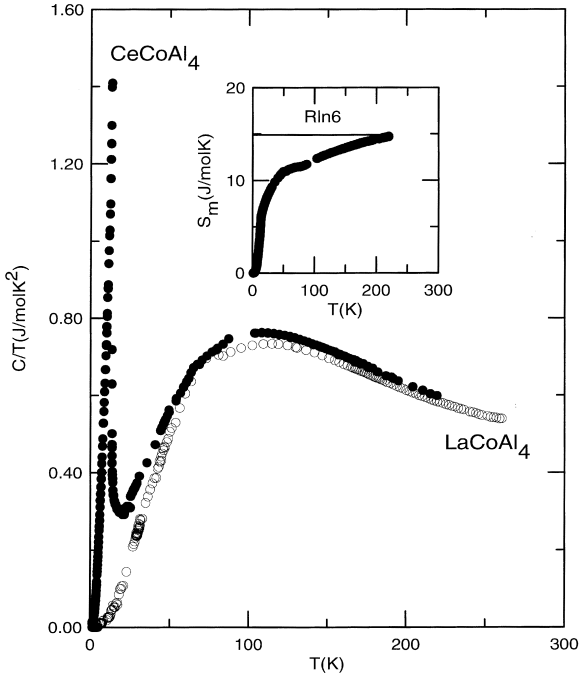

Fig. 1. C/T vs T of $CeCoAl_4$ (full circle symbols) and $LaCoAl_4$ (open circle symbols) measured in zero field. The inset shows the temperature dependence of the magnetic entropy of $CeCoAl_4$.

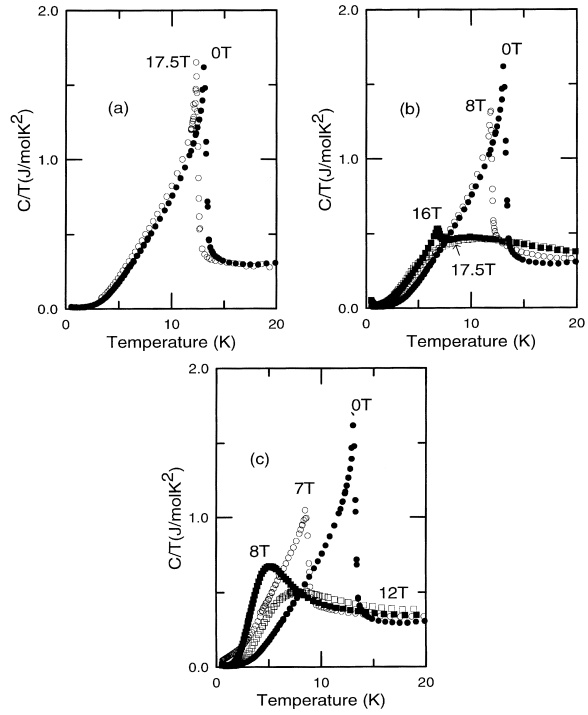

Fig. 2. C/T vs T of $CeCoAl_4$ measured in different fields. (a): For fields applied along the a-axis. (b): For fields applied along the b-axis. (c): For fields applied along the c-axis.

At low temperature, the specific heat still deviates from the law: $C/T=\gamma+\beta T^2$. This deviation can be attributed to the tail of the magnetic peak. In (high) fields, moreover, we observed an upturn at very low temperature (<1 K). This upturn might be associated with the nuclear contribution (presumably from Co and Al atoms) because it strongly increases and shifts towards higher temperature with increasing magnetic field. Although it is difficult to obtain an exact value of γ, we would like to mention here that in zero field γ ranges from 5–10 $mJ\,mol^{-1}K^{-2}$ which is rather low in comparison with other ternary Ce-based compounds (see, for instance, Ref. [7]).

The field dependence of T_N of $CeCoAl_4$ is drawn in Fig. 3. In this figure, for comparison, we also added the data obtained from the $M(T)$ measurements. The anisotropic character is evident: T_N is strongly field dependent for fields applied along the b- and the c-axes, and hardly field dependent for fields applied along the a-axis.

Based on the magnetic measurements [2], it was already pointed out that in $CeCoAl_4$, up to fields of 20 T, the ground state is far from being a pure $|5/2>$ state. From the susceptibility measurements presented in ref. [2], we infer

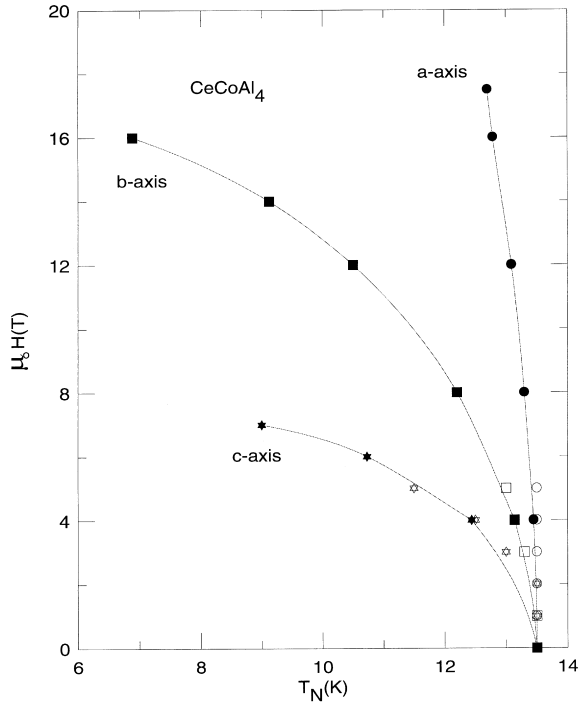

Fig. 3. Field dependence of T_N for $CeCoAl_4$ (open symbols represent the data taken from $M(T)$; full symbols represent the data taken from $C(T)$ measurements).

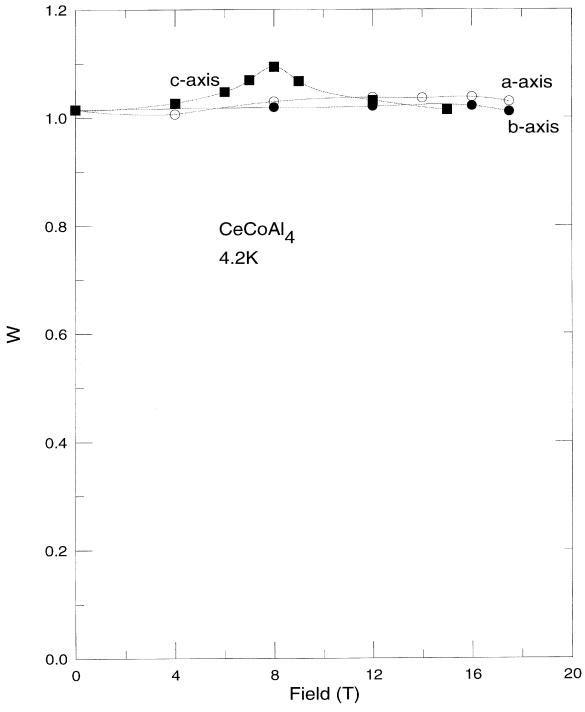

Fig. 4. The number of available states, W, as a function of the applied field for $CeCoAl_4$ at 4.2 K.

that the a-axis is the 'difficult axis for the magnetisation', i.e. the (b, c) plane is, in first approximation, an easy plane. Therefore, we take the a-axis as the quantisation axis. In that representation, the ground state (in the absence of an effective field) is expected to be quite near a doublet $|\pm 1/2>$. In the orthorhombic symmetry the in-plane anisotropy, i.e. the crystal field coefficient B_2^2, will induce some mixing with the other states. The result is that the moment is oriented along the (easy) c-axis, the magnitude of the moment being near 1.29 μ_B (in the $|+1/2>$, $|-1/2>$ subspace). In the antiferromagnetic arrangement, however, substantial molecular fields are present, including considerable mixing with the other states. Also the possibility of level crossing should be kept in mind. The application of an external field in the a- or b-directions will gradually 'bend' the antiferromagnetically oriented moments from the (negative or positive) c-direction towards the field direction. Although the effective field acting on the Ce-4f shell is not expected to change too much, level crossing cannot be ruled out. When the field is applied in the c-direction, however, the effective field acting on one sublattice may increase, whereas that acting on the oppositely oriented sublattice may decrease (so approaching the unsplit doublet). In order to investigate the occurrence of level crossing (including the effect of the approach towards the unsplit doublet), we present in Fig. 4 the number of available states, W, as a function of the applied field at 4.2 K for $CeCoAl_4$. In this figure W is defined by the relation $S_m = R\ln W$, i.e. $W = \exp(S_m/R)$. Along the a- and the b-axes, W is almost unchanged with increasing field up to 17.5 T. Along the c-axis, a (small) maximum is reached at 8 T with $W \cong 1.1$. However, the values of W in different fields along a-, b- and c-axes are (very) close to 1. this can be taken as an indication that at 4.2 K, level crossing does not occur for fields applied along the main axes at least up to 17.5 T. The slight increase of W observed when the field is applied in the c-direction can be ascribed to the approach to the 'unsplit doublet'.

4. Conclusions

In summary, the results of our present investigation of the specific heat have revealed anisotropic properties of $CeCoAl_4$. These results are in good agreement with the results of magnetisation measurements for $CeCoAl_4$. Neutron diffraction measurements in the magnetically ordered state as well as calculations involving the search for suitable crystalline electric field parameters are in progress.

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