Neutron-diffraction study of $CeCuGa_3$

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Neutron-diffraction experiments have been performed on both polycrystalline and single-crystal samples of $CeCuGa_3$. The results of the powder diffraction experiments show that $CeCuGa_3$ adopts an incommensurate magnetic structure at 1.25 K. The propagation wave vector associated with the magnetic ordering k_m is (0.176, 0.176, 0), and the magnitude of the magnetic moment in the ordered state is $1.24 \pm 0.02 \mu_B$. Single-crystal neutron diffraction confirmed the existence of magnetic satellite peaks at Q values determined by the wave vector k_m. Additional satellites have been observed in the single-crystal diffraction experiments with an incommensurate propagation vector of $k_s = (0.137, 0.137, 0)$. These are probably the result of a short-ranged modulation of the crystal structure. [S0163-1829(98)05014-0]

I. INTRODUCTION

The series of alloys $CeCu_xAl_{4-x}$, and CeM_xGa_{4-x}, where M is one of the *d-block* metals Au, Cu, Ni, or Pt, have been the subject of a number of recent experimental investigations (Refs. 1–7, and references therein). These alloys have a solubility range for x between 0.5 and 1.5, and outside this range the samples are multiphase. The electrical and magnetic properties of these materials are governed by the relative strength of the competing interactions of the Kondo effect and the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. By decreasing the value of x in these series of alloys, the strength of the RKKY exchange interaction is increased with respect to the Kondo effect, leading to higher ordering temperatures of these compounds. With the exceptions of $CePtGa_3$ and $CeNiGa_3$ the aforementioned compounds crystallize with a tetragonal structure, with the space group dependent upon the value of x. The compound $CePtGa_3$ crystallizes in the orthorhombic $PrNiGa_3$ ($Fmmm$) structure,[6] while the structure of $CeNiGa_3$ is sensitive to its heat treatment. An as-cast sample of $CeNiGa_3$ forms in a body-centered tetragonal structure that reverts to the orthorhombic structure after annealing at 700 °C for six days.[7] This change in structure of $CeNiGa_3$ considerably broadens the magnetic transition as seen from measurements of the specific heat.[7]

The compound $CeCuGa_3$ crystallizes in the $BaNiSr_3$-type structure ($I4mm$). Our own measurements of the ac susceptibility and specific heat of polycrystalline $CeCuGa_3$ have shown the onset of a magnetic transition at approximately 1.9 K.[5] The entropy associated with the transition into the magnetically ordered state only attains a value of 2.58 J mol^{-1} at the ordering temperature, which is significantly lower than the theoretical value for a ground-state doublet of R ln2 ($\approx$5.76) J mol^{-1}. The additional magnetic entropy is spread over a wide temperature range, which is typically caused by a combination of the Kondo effect and short-ranged order. In this paper we present results of neutron-diffraction measurements from polycrystalline and single-crystal samples that show the existence of long-range incommensurate magnetic order in $CeCuGa_3$ below its ordering temperature, and the possibility of a structural modulation within the crystal.

II. EXPERIMENTAL DETAILS

Approximately 30 g of polycrystalline $CeCuGa_3$ were prepared by arc melting the stoichiometric quantities of the constituent elements (Ce 99.9%; Cu, Ga 99.99%) in a titanium gettered argon atmosphere. The weight losses due to the arc-melting process were negligible ($<$0.1%). The material was then wrapped in tantalum foil and annealed in Ar purged quartz tubes for two weeks at 600 °C. X-ray powder diffraction and energy dispersive spectroscopy measurements showed the sample was single phase. A single crystal of $CeCuGa_3$, of volume approximately 4 cm^3, was grown at the University of Birmingham using the Czochralski method in a tungsten crucible.

Neutron powder diffraction experiments were performed using the two-axis diffractometer D1B at the Institut Laue-Langevin in Grenoble. The polycrystalline samples were powdered and placed into a vanadium can and mounted in a He cryostat with a base temperature of 1.25 K. Neutron-diffraction measurements on the single crystal of $CeCuGa_3$ were taken on the triple-axis spectrometer HB 2 at the high-flux-isotope reactor at the Oak Ridge National Laboratory,

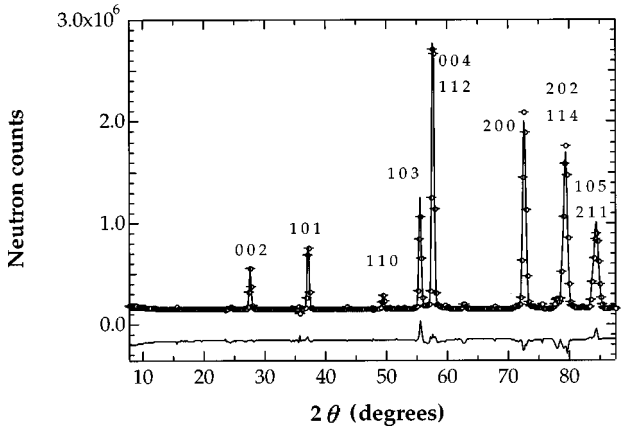

FIG. 1. The FULLPROF refinement of polycrystalline $CeCuGa_3$ assuming the $BaNiSn_3$ structure ($I4mm$ space group). The observed neutron diffraction spectrum at 10 K is shown by the markers, while the fit is shown by the solid line. The difference between the observed and calculated data is shown underneath the plot.

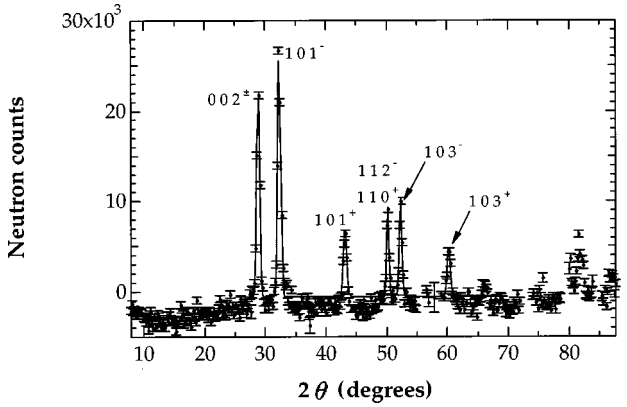

FIG. 2. The difference between the neutron diffraction spectra taken at 1.25 and 10 K for polycrystalline $CeCuGa_3$ showing the magnetic diffraction peaks. The calculated fit is shown by the solid line. Note: the points close to the nuclear Bragg peaks have been removed for clarity, and the group of peaks near 80° have been ignored due to close proximity of the (202) and (114) Bragg peaks.

using an incident wavelength of 2.351 Å, up to a $|Q|$ value of approximately 4.2 $Å^{-1}$. PG [0 0 2] was used as the monochromator and analyzer, and as a filter to minimize the contamination from the λ/2 in the incident beam. The single crystal was mounted inside a He cryostat with a base temperature of approximately 1.9 K with the [1 1 0] axis vertical, allowing access to the Bragg reflections in the $[h\,h\,l]$ plane.

III. RESULTS

A. Powder neutron diffraction

Neutron-diffraction spectra of the polycrystalline sample were recorded at temperatures of 10 K in the paramagnetic state, and in the ordered state at 1.25 K using an incident wavelength λ of 2.52 Å. Both sets of nuclear Bragg diffraction peaks could be indexed assuming a tetragonal $BaNiSn_3$-type crystal structure ($I4mm$). The crystal structure at 10 K was refined by Rietveld analysis using the FULLPROF program,[8] assuming the $I4mm$ space group. The calculated and observed neutron-diffraction spectrums are shown in Fig. 1. The final structural parameters for $CeCuGa_3$ are shown in Table I. At 10 K the refined lattice parameters were at 10 K $a=4.245\pm0.006$ Å, and $c=10.42\pm0.01$ Å, with R factors of $R_{wp}=7.47\%$, $R_p=5.14\%$, and $R_{\exp}=3.3\%$. Within experimental error no discernible difference was found between the structural parameters at 1.25 and 10 K. The difference between the two diffraction patterns at 10 and 1.25 K, shown in Fig. 2, reveals six magnetic diffraction peaks which are incommensurate with the chemical cell.[9] These magnetic Bragg reflections can be indexed in terms of $|Q|=|\tau_{hkl}\pm k_m|$, where τ_{hkl} is a reciprocal lattice vector of the chemical unit cell and k_m is the propagation vector of the magnetic ordering. Trial and error initially determined $k_m=(0.176, 0.176, 0)$. The best fit to the integrated intensities was obtained assuming a simple helical structure for the magnetic moments. For such a helical arrangement the integrated intensities of the magnetic Bragg peaks (in barns unit $cell^{-1}$) is given by[10,11]

$$I_M(|\mathbf{Q}|)=\frac{P_M}{4}\langle 1+\cos^2\,\eta\rangle|F_M(|\mathbf{Q}|)|^2$$

with p_m the multiplicity of the magnetic Bragg peak, and η is the inclination of the spiral axis to the scattering vector $\mathbf{Q}$. The term $\langle 1+\cos^2\,\eta\rangle$ is the average of $(1+\cos^2\,\eta)$ over all equivalent scattering vectors, and the magnetic structure factor $F_M(|Q|)$ is given by[12]

$$|F_M(|\mathbf{Q}|)|^2\propto\left[p\sum_j\,|f_j(\mathbf{Q})\langle\mu_j\rangle e^{i\mathbf{Q}\cdot\mathbf{r_j}}|\right]^2,$$

where $f_j(Q)$ is the magnetic form factor of the Ce^{3+} ion,[11] $\mathbf{r_j}$ is the position of the magnetic ions in the unit cell of average magnetic moment $\langle\mu_j\rangle$, and p is a numerical constant equal to 2.7 fm. For a crystallographic structure with tetragonal symmetry the orientation of the axis of the spiral to the c axis φ, can be determined using

$$\langle\cos^2\,\eta\rangle=\{\tfrac{1}{2}(h^2+k^2)\mathbf{a}^{*2}\,\sin^2\,\varphi+\mathbf{c}^{*2}\,\cos^2\,\varphi\}d^2,$$

where $\mathbf{a}^*$, and $\mathbf{c}^*$ are the reciprocal lattice vectors, and d is the d-spacing of the $[h\,k\,l]$ Bragg reflection.[13] The comparison between the calculated and integrated intensities assuming a simple spiral arrangement of the magnetic moments is shown in Table II. The best-fit produces a value of $1.24\pm0.02\mu_B$ for the magnitude of the magnetic moment at 1.25 K, and an orientation of the spiral axis to the c axis of 35° ±2°, close to the body diagonal of the crystallographic structure (≈30°).

TABLE I. The structural parameters of $CeCuGa_3$ at 10 K refined from the neutron powder diffraction spectrum at 10 K assuming the $I4mm$ space group. Estimated standard deviations of the fit are given in parentheses.

Atom	Site	x/a	y/a	z/a	B (Å^2)
Ce	$2a$	0	0	0	1.2(2)
Cu	$2a$	0	0	0.6129(6)	0.9(1)
Ga(1)	$2a$	0	0	0.3871(6)	0.7(1)
Ga(2)	$4b$	0	$\frac{1}{2}$	$\frac{1}{4}$	1.5(2)

TABLE II. A comparison of the calculated and observed values of the integrated intensities I_{calc} and I_{obs} (in barns per Ce^{3+} ion), and the calculated and observed positions of the magnetic diffraction peaks θ_{calc} and θ_{obs}, of polycrystalline $CeCuGa_3$. The $(1\,1\,0)^-$ peak was too weak to be observed, while the $(0\,0\,4)^{\pm}$, $(-1\,1\,2)^-$, and $(1\,1\,0)^+$ are masked by the strong (0 0 4) and (1 1 2) nuclear Bragg peaks.

$(h\,k\,l)$	θ_{obs}	θ_{calc}	I_{obs}	I_{calc}
$(0\,0\,2)^{\pm}$	14.42	14.55	0.153	0.157
$(1\,0\,1)^-$	16.16	16.13	0.252	0.253
$(1\,1\,0)^-$		20.25		0.06
$(1\,0\,1)^+$	21.60	21.84	0.19	0.22
$(1\,1\,2)^-$	24.74	24.95	0.20	0.17
$(1\,-1\,0)^+$				
$(1\,0\,3)^-$	26.12	26.09	0.25	0.19
$(1\,0\,3)^+$	30.10	30.31	0.18	0.13

B. Single-crystal neutron diffraction

A typical neutron-diffraction scan performed on the single crystal of $CeCuGa_3$ in the $[h\,h\,l]$-plane of reciprocal space, using an incident wavelength λ of 2.352 Å, is shown in Fig. 3. At 2 K the scan along the $[h\,h\,0]$ direction around the (1 1 0) Bragg peak shows four incommensurate satellite peaks. Each pair of satellite peaks can be indexed using either the propagation vectors $k_1=(0.176,0.176,0)$, or $k_2=(0.137,0.137,0)$. The set of peaks described by k_1 are obviously the same as those described by k_m for the polycrystalline sample, which are caused by long-range magnetic order. Figure 4 shows a temperature scan of the $(1\,1\,2)^-$ magnetic Bragg peak that indicates the onset of magnetic ordering to be around 4 K, although this is different to the 1.9 K observed for the peak position of the ac susceptibility signal[5] it agrees well with the specific-heat measurements shown in the lower part of this figure. The extra contribution observed in the specific heat at lower temperatures is probably the result of a Schottky anomaly caused by splitting of the ground state by the crystalline electric field.

The set of satellites described by k_2 remain unchanged in intensity and position between 1.9 and 300 K, the temperature range over which scans were recorded. In contrast to the width of the magnetic and commensurate nuclear Bragg peaks, which are resolution limited, the peaks represented by

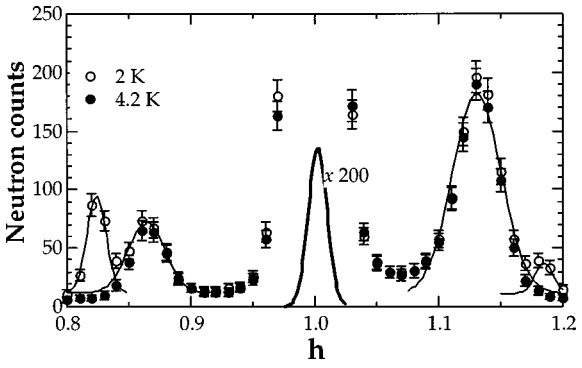

FIG. 3. A Q scan performed on a single crystal of $CeCuGa_3$ along the $[h\,h\,0]$ direction around the (1 1 0) Bragg peak. Two sets of incommensurate Bragg peaks can be observed at 1.9 K.

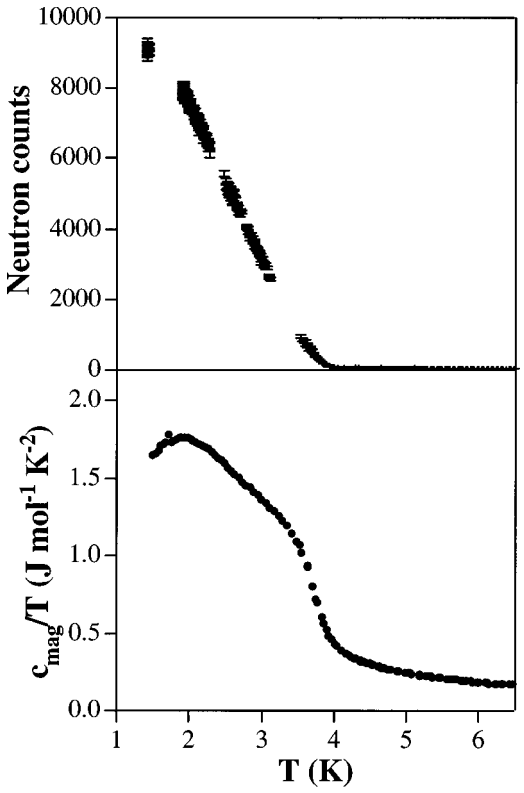

FIG. 4. A low-temperature scan of the $(1\,1\,2)^-$ magnetic Bragg peak, and the low-temperature specific heat of $CeCuGa_3$ taken from Ref. 5.

k_2 are not. These peaks have a half width at half maximum of 0.043 ± 0.002 Å^{-1}, which corresponds to a correlation length of approximately 310 Å. These satellites do not show the drop in intensity with increasing $|Q|$ as expected for magnetic diffraction peaks, because of the magnetic form factor $f_j(Q)$, if these peaks were the result of magnetic ordering of the Cu ions above 300 K. All this leads us to assume that these peaks are caused by a structural modulation of the crystal structure, which is short ranged, leading to an intrinsic width for these structural peaks.

IV. DISCUSSION

Neutron-diffraction measurements presented in this paper, have confirmed the presence of long-range incommensurate magnetic order in $CeCuGa_3$. The results indicate that the most likely structure adopted by the magnetic moments is a simple helical arrangement, with a magnetic moment of magnitude $1.24\mu_B\pm0.02\mu_B$ at 1.25 K, and a propagation vector of (0.176, 0.176, 0). This propagation vector does not vary over the temperature range of this study. Although the bulk and transport properties of $CeCuGa_3$ seem to indicate the Kondo effect may be responsible for at least part of the reduction of the ordered moment when compared to the free Ce^{3+} moment ($2.51\mu_B$) it is possible that this discrepancy is caused by crystalline electric-field splitting of the $J=\frac{5}{2}$ multiplet. Only by determining the crystal-field parameters can the exact cause of the reduced moment in the ordered state be found.

An additional set of incommensurate satellites have been observed with an incommensurate wave vector of

(0.136, 0.136, 0). This initial study indicates that they are the result of a short-range structural modulation. There are many types of modulated structure that can cause these incommensurate satellites, see for instance.[14] In this case it appears that these peaks are caused by a displacive modulation of the atomic position, and/or a modulation of composition or atomic occupation probability. The occurrence of a displacive modulation indicates the tendency towards a structural phase transition, which has been observed for $CeNiGa_3$, where there is a transformation from a tetragonal structure in the as-cast sample to an orthorhombic structure on annealing at 900 °C. This structural transformation significantly broadens the magnetic transition at the ordering temperature as observed in measurements of specific heat.[7] At the moment a careful metallographic examination, using electron diffraction and transmission electron microscopy, is being undertaken to try and determine the effect of a prolonged annealing treatment on the incommensurate satellites in $CeCuGa_3$. The existence of the structural modulation lowers the local crystal symmetry, and may well split the $|\pm\frac{1}{2}\rangle$ ground-state doublet (expected for a Ce ion in tetragonal symmetry) producing a Schottky anomaly in the specific heat. This may be the cause of the broadened transition near the ordering temperature already observed,[5] which would require a splitting of approximately 0.2 meV between the ground state and first excited state. Experiments are also planned to investigate if any coupling between the magnetic ordering and the structural modulation occurs, as they both have the same directional dependence.

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