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MAGNETIC PROPERTIES AND MAGNETIC STRUCTURE OF $CeAl_2Ga_2$

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Magnetic properties of the tetragonal compound $CeAl_2Ga_2$ were investigated by means of electrical resistivity, specific heat, magnetization and neutron diffraction measurements on polycrystalline samples. Cerium behaves as a normal Ce^{3+} ion, with indication of a very weak Kondo effect. Magnetization and neutron measurements show that this compound presents a quite original magnetic structure below $T_N = 9$ K, i.e. a long-period commensurate collinear structure with a wave vector $\boldsymbol{k} = (0, 0, k)$ where $k = 6/13$, corresponding to a $(++--+++--++--)$ sequence of the Ce moments which are perpendicular to the 4-fold axis. This structure accounts for the small ferromagnetic and the large antiferromagnetic components observed within the basal plane.

1. Introduction

The ternary $RM_2M'_2$ compounds (R = rare-earth, M = 3d, 4d or 5d transition metal, M′ = Si or Ge), with the tetragonal $ThCr_2Si_2$-type structure (space group I4/mmm) constitute a large family of compounds which have been extensively studied for the last few years [1–3]. In the cerium-based compounds, many interesting properties have been found, such as superconductivity, valence fluctuations, Kondo effect and heavy fermion behaviour [4–7]. Few compounds with the same formula, where M is not a transition metal, have been reported to crystallize in the same type of structure. The compound $CeAl_2Ga_2$ belongs to this category [8], and in this respect is worthy of study.

We have undertaken the study of the magnetic properties of $CeAl_2Ga_2$ together with the isomorphous non-magnetic compound $LaAl_2Ga_2$. Both polycrystalline materials were prepared by the fusion of stoichiometric amounts of the constituents in an induction furnace. The ingots were then annealed at 800 °C for one week. X-ray power patterns indicated the single-phase character of the samples. In this paper, the results of resistivity (section 2), specific heat (section 3), magnetization (section 4) and neutron diffraction (section 5) experiments are reported. Section 6 is devoted to a discussion of the results which give evidence for competition between crystal field, Kondo effect and exchange interactions.

2. Resistivity measurements

The resistivity of $CeAl_2Ga_2$ and $LaAl_2Ga_2$ has been measured between 1.5 and 300 K using an ac four-probe method (see fig. 1). The anomaly occurring around 8.5 K in $CeAl_2Ga_2$ is attributed to the appearance of an antiferromagnetic ordering, according to the magnetic properties described below. The temperature variation of the resistivity of $LaAl_2Ga_2$ presents a typical lattice behaviour with a Debye temperature $\Theta_D = 192$ K. After

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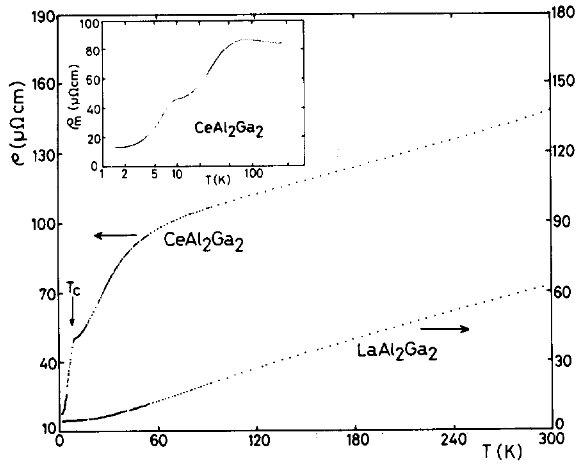

Fig. 1. Temperature dependence of the electrical resistivities of $CeAl_2Ga_2$ and $LaAl_2Ga_2$. Inset: temperature dependence of the magnetic part of the resistivity of $CeAl_2Ga_2$ in a semi-logarithmic scale.

correction for this lattice contribution, the magnetic part of the resistivity, ρ_m, of $CeAl_2Ga_2$ shows a small logarithmic decrease above 100 K which could be attributed to a weak Kondo effect (inset in fig. 1). Note that this decrease could be also explained by a slight overestimation of the lattice contribution in $CeAl_2Ga_2$. Just above 8.5 K, there is no minimum as frequently observed in Kondo systems, but rather a positive curvature is present.

3. Specific heat

The specific heat C_p of $CeAl_2Ga$ in the temperature range 1.45–30 K was measured in a fully automated Nernst calorimeter (see fig. 2). A λ-type anomaly is observed, at a temperature consistent with the ordering temperature of 8.5 K found from resistivity measurements. For temperatures larger than 11 K, the extrapolation of C_p/T vs. T^2 yields a γ value of (80 ± 10) mJ/mol K^2. This value is of the same order of magnitude as that generally observed in magnetically ordered Kondo lattices. The magnetic contribution to the specific heat C_m has been obtained by subtracting the normal electronic and the phonon parts from the total heat capacity: C_m [mJ/mol K] $= C_p - 5.0T - 0.60T^3$. In this expression the assumed electronic contribution (5.0 mJ/mol K) was taken as that generally observed in La-based compounds. The magnetic entropy S is then deduced as a function of temperature (inset in fig. 2). The value evaluated at the magnetic transition temperature is 4.9 J/mol K. This is 85% of the value expected for a doublet ground state, $S = R \ln 2 = 5.76$ J/mol K, this latter value being reached at about 14 K. The reduced entropy at T_N may be mainly accounted for by the existence of magnetic correlations just above the ordering temperature and possibly by the presence of a weak Kondo effect.

4. Magnetization measurements

Bulk magnetization measurements were performed by using the extraction method in magnetic fields up to 80 kOe and in the temperature range 1.5–300 K.

The temperature dependence of the reciprocal susceptibility follows a Curie–Weiss law above 55 K (fig. 3), leading to an effective paramagnetic moment $\mu_p = 2.51\mu_B$, a value very close to the free Ce^{3+} ion value, and to a negative paramagnetic Curie temperature $\Theta_p = -17$ K. At low tempera-

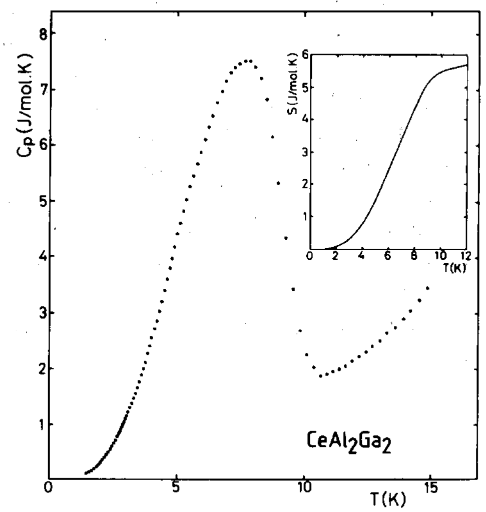

Fig. 2. Temperature dependence of the heat capacity C_p of $CeAl_2Ga_2$ at low temperature. Inset: temperature dependence of the magnetic entropy S of $CeAl_2Ga$ at low temperature.

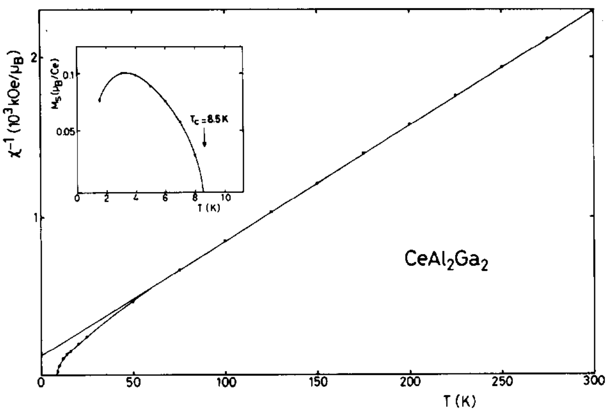

Fig. 3. Temperature dependence of the reciprocal susceptibility of $CeAl_2Ga_2$. Inset: temperature dependence of the spontaneous magnetization.

ture, the reciprocal susceptibility deviates from the Curie–Weiss law and becomes nearly zero at the ordering temperature $T_N = (8.5 \pm 0.5)$ K.

Several isothermal magnetization curves are reported in fig. 4 in the low temperature range. Below T_N and especially at 1.5 and 3 K the isotherms exhibit two different characteristic regimes: i) in low field a ferromagnetic behaviour is observed, the spontaneous magnetization deduced from Arrott plots is small and is reported as a function of temperature in the inset of fig. 3. Note that below 3 K this spontaneous magnetization decreases very weakly. ii) A metamagnetic transition occurs in higher fields (around 35 kOe at 1.5 K); the critical field is weakly temperature dependent and the transition disappears around 7 K.

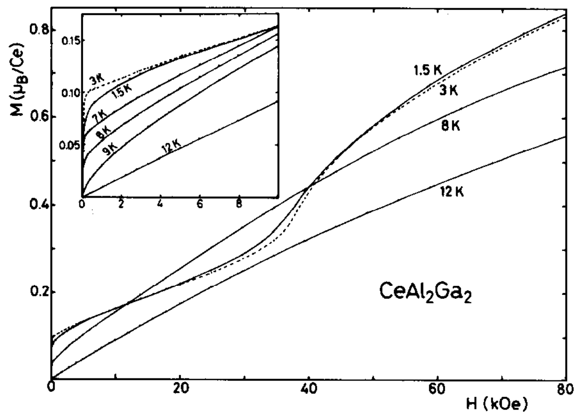

Fig. 4. Isothermal magnetization curves in $CeAl_2Ga_2$. Inset: detail of the low field region.

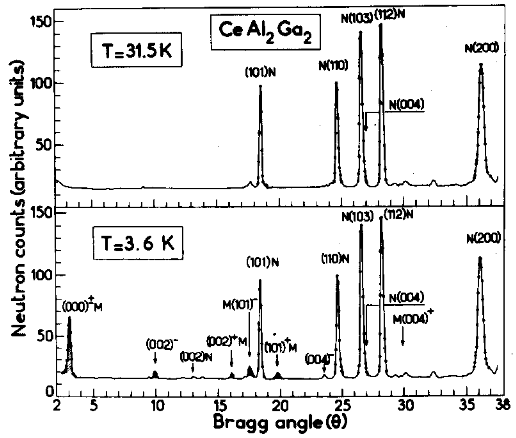

Fig. 5. Neutron diffraction patterns performed on $CeAl_2Ga_2$ at 31.5 and 3.6 K.

5. Neutron diffraction results

Neutron diffraction measurements were carried out on a position sensitive detector [9] installed on a thermal beam in the Siloe reactor at the Centre d'Etudes Nucléaires in Grenoble. The neutron wavelength was $\lambda = 2.483$ Å. The $CeAl_2Ga_2$ polycrystalline ingot was reduced in powder in order to avoid preferred orientations.

The pattern recorded at 31.5 K (see fig. 5) indicates that the sample was of good quality as only Bragg peaks associated with the body-centered tetragonal structure (space group I4/mmm) were observed. Without taking into account of the lattice translations, this crystal structure of $ThCr_2Si_2$-type contains one $CeAl_2Ga_2$ with:

- one Ce^{3+} ion in the site 2a at (0 0 0),
- two Al atoms in the site 4d at (0 1/2 1/4) and (1/2 0 1/4),
- two Ga atoms in the site 4e at (0 0 z) and (0 0 $\bar{z}$).

The positions and the integrated intensities of a few nuclear Bragg peaks were used to characterize the crystal structure. At 31.5 K, the lattice parameters are $a = (4.203 \pm 0.003)$ Å and $c = (10.955 \pm 0.002)$ Å. Using the scattering lengths $b_{Ce} = 0.476$,

$b_{Al} = 0.345$ and $b_{Ga} = 0.720$ (in 10^{-12} cm), the best fit to the experimental data yields to a value $z = 0.387$ with a reliability factor $R = 8\%$ (see table 1). Then the structure consists in a stacking of (001) atomic planes, according to a sequence Ce–Ga–Al–Ga–Ce, located at $z = 0$, $1/2 - z_{Ga} = 0.113$, $1/4$, $z_{Ga} = 0.387$ and $1/2$, respectively. Another important result is that there is no evidence for any mixing between the Al and Ga sites.

Patterns recorded at low temperatures (see fig. 5) give evidence for several superlattice magnetic peaks indicating the existence of a magnetic ordering. The scattering vector moduli, deduced from these peak positions, can be accounted for by a single wave vector $\boldsymbol{k} = (0, 0, k)$ with $k = 0.458 \pm 0.003$. We remember that magnetic scattering vectors $\boldsymbol{h}$ are defined by the relation $\boldsymbol{h} = \boldsymbol{H} + \boldsymbol{k}$, where $\boldsymbol{H}$ spans the various Brillouin zone centres of the nuclear lattice. The wave vector value was found to be temperature independent. The intensities of the superlattice peaks (0 0 k) and (0 0 $2-k$) were investigated as a function of temperature (see fig. 6) yielding an ordering temperature $T_N = (9 \pm 1)$ K.

As the unit cell contains one Ce^{3+} Bravais lattice (b.c.t.), the coupling between magnetic moments is fully determined by the knowledge of the wave vector. The observed wave vector thus indicates that the magnetic ordering in $CeAl_2Ga_2$ consists in a stacking of ferromagnetic (001) planes with either a helimagnetic or an amplitude modulated structure. A comparison between these two possibilities may be carried out from the observed intensities. First of all we have to notice that the

Table 1
Observed and calculated intensities of a few nuclear Bragg peaks of $CeAl_2Ga_2$ measured at 31.5 K. Intensities are given in barns per $CeAl_2Ga_2$ unit

$h\,k\,l$	I_{obs} (barn)	I_{cal} (barn)
0 0 2	0.036	0.025
1 0 1	3.13	3.07
1 1 0	6.16	5.91
1 0 3 0 0 4	12.04	12.14
1 1 2	14.44	15.67
2 0 0	30.67	27.5
1 1 4	18.60	20.28

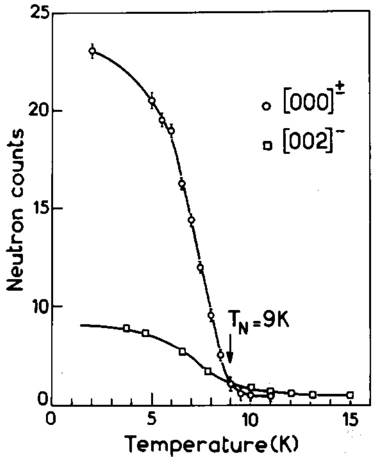

Fig. 6. Temperature dependence of the (0 0 k) and (0 0 $2-k$) superlattice peaks in $CeAl_2Ga_2$.

existence of intensities for (0 0 k) and (0 0 $2-k$) implies that the magnetic moment direction lies within the basal plane. If $\hat{u}$ and $\hat{w}$ are unit vectors within the basal plane and along the c-axis, respectively, the intensity can be written as [10]:

$$I(\boldsymbol{h} = \boldsymbol{H} + k) = p(0.27)^2 f^2(\theta) \frac{m_0^2}{4} \left(1 + \frac{(\hat{w} \cdot \boldsymbol{h})^2}{\boldsymbol{h}^2}\right)$$

for a helimagnetic structure, and:

$$I(\boldsymbol{h} = \boldsymbol{H} + \boldsymbol{k}) = p(0.27)^2 f^2(\theta) \frac{A_k^2}{4} \left(1 - \frac{(\hat{u} \cdot \boldsymbol{h})^2}{\boldsymbol{h}^2}\right)$$

for a modulated structure, where p is the multiplicity of the peak, $f(\theta)$ the form factor, m_0 the moment value and A_k the amplitude of the modulation.

However, in the latter case, there are two possible moment directions in the basal plane giving rise to two S-type domains. Thus, we have to replace $(1 - (\hat{u} \cdot \boldsymbol{h})^2/\boldsymbol{h}^2)$ by the average $\frac{1}{2}[(1 - \hat{u} \cdot \boldsymbol{h})^2/\boldsymbol{h}^2 + (1 - \hat{v} \cdot \boldsymbol{h})^2/\boldsymbol{h}^2]$ ($\hat{v}$ being perpendicular to $\hat{u}$) which is nothing but $\frac{1}{2}[(1 + \hat{w} \cdot \boldsymbol{h})^2/\boldsymbol{h}^2]$. Therefore, the helimagnetic and the modulated structures give the same intensities, the only difference being the magnitude of the magnetic moment. In the case of a sinusoidal modulation the moment amplitude would be $A_k = \sqrt{2}\, m_0$, i.e. a factor $\sqrt{2}$ larger than the moment value in the helimagnetic structure. A comparison between ob-

Table 2
Observed and calculated magnetic intensities of $CeAl_2Ga_2$ at $T = 3.6$ K in barns per Ce^{3+}

$h = H \pm k$	I_{obs} (barn)	I_{cal} (barn)
$(0\,0\,0)^{\pm}$	0.099	0.104
$(0\,0\,2)^{-}$	0.112	0.100
$(0\,0\,2)^{+}$	0.098	0.095
$(1\,0\,1)^{-}$	0.213	0.192
$(1\,0\,1)^{+}$	0.251	0.221
$(0\,0\,4)^{-}$	0.078	0.078
$(1\,1\,0)^{\pm}$ $(1\,0\,3)^{-}$	0.405	0.397
$(1\,0\,3)^{+}$	0.201	0.25
$(1\,1\,2)^{-}$	0.250	0.190
$(1\,1\,2)^{+}$ $(0\,0\,4)^{+}$	0.267	0.267

served and calculated magnetic intensities, given in table 2, yields a reliability factor of 15%. For magnetic moments within the basal plane we determined a moment value of $(1.18 \pm 0.07)\mu_B$ in the case of a helimagnetic structure while in the case of a sinusoidal modulation the amplitude is $(1.7 \pm 0.1)\mu_B$. In the case of the helimagnetic structure, magnetic moments rotate by about 82° from plane to plane when moving along the c-axis. In the case of a sinusoidal modulation, moments are aligned along a well-defined direction in the basal plane and the moment value is modulated when moving along the c-axis. Due to the existence of domains this direction cannot be determined from a powder experiment.

Note that the ferromagnetic component observed by magnetization measurements was not detected because it should lead to a negligible contribution to the nuclear peaks. A more complete description of the magnetic structure will be discussed below in relation to all the magnetic properties.

6. Discussion

The measurements presented in this paper show that the Kondo effect, if present, is weak in $CeAl_2Ga_2$. Indeed, the decrease of $\rho_m(T)$ at high temperature is small and there is no noticeable reduction of the magnetic entropy at low temperature. Actually, Ce in $CeAl_2Ga_2$ seems rather normal if we consider that no reduction of the ce moment is observed (see below).

Preliminary magnetic measurements on a single crystal show that i) the crystal field ground state is the $|\pm 1/2\rangle$ doublet and ii) the ferromagnetic as well as the antiferromagnetic components are within the basal plane, i.e. perpendicular to the c-axis. Note that the value of the ferromagnetic component measured on a single crystal is quite consistent with that measured on a polycrystalline sample.

With these elements we can discuss the possible magnetic structures of $CeAl_2Ga_2$. Due to the weakness of the ferromagnetic component, we discuss first the main contribution, namely the antiferromagnetic one. A $|\pm 1/2\rangle$ ground state doublet is associated with a magnetic moment of $1.27\mu_B$ within the basal plane. This is consistent with both structures described above. Indeed, for the helimagnetic structure the experimental moment reaches $(1.18 \pm 0.07)\mu_B$/Ce. Just as for the collinear sine wave structure, the actual structure at low temperature must be of antiphase-type, i.e. with equal moments, because of the magnetic character of the ground state. In that case, the observed value of $(1.7 \pm 0.1)\mu_B$/Ce corresponds to the amplitude of the first harmonic A_k, which is related to the actual magnetic moment m_0 by the relation $A_k = (4/\pi)m_0$. Here, we get a moment value $m_0 = (1.3 \pm 1)\mu_B$/Ce, in good agreement with that of the $|\pm 1/2\rangle$ ground state.

The presence of the weak ferromagnetic component in the basal plane is surprising. Several assumptions can explain it:

i) there are two independent phases, a ferromagnetic and an antiferromagnetic phase with almost the same energy. This possibility is rather unlikely, as the value of the ferromagnetic contribution is sample-independent.
ii) the magnetic structure is the sum of both components. However, that would lead to rather complex and unusual situations if the assumption of a true incommensurate wave vector is retained,
iii) a third hypothesis which reconciles all the observed magnetic properties is that the wave

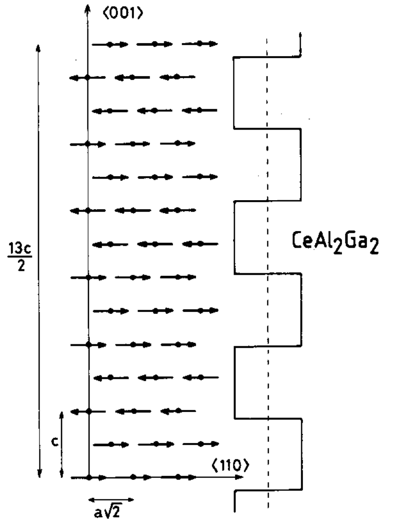

Fig. 7. Magnetic structure of $CeAl_2Ga_2$.

vector is locked on a commensurate value such as $k = 6/13$, very close to the value given above. Considering the collinear structure at low temperature, the associated sequence of constant magnetic moment is $(++--+++--++--)$, that naturally leads to a net ferromagnetic component $\frac{1}{13}m_0 \approx 0.1\mu_B$, in close agreement with the observed value. This structure, shown in fig. 7, is rather similar to that of pure thulium [11,12] or one of the magnetic phases of CeSb [13]. Note that the decrease of the spontaneous magnetization below 3 K can originate from unusual magnetization processes associated with this complex magnetic structure. The nature of the anisotropy interactions between the planes perpendicular to the c-axis that leads to the observed structure remains to be explained.

In the case of the helimagnetic structure, the phase variation of the magnetic moments should be locked at $\pi/2$ from plane to plane, with the same type of fault as above, i.e. two adjacent planes with parallel moments within each sequence of 13 planes. However, this structure seems less likely than the previous one.

Neutron diffraction experiments on a single crystal have to be performed in order to clarify the exact magnetic ordering of this quite interesting compound.

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