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MAGNETIC PROPERTIES OF CeCuSi

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The ternary hexagonal compound CeCuSi has been studied by resistivity, neutron diffraction and magnetization measurements. It exhibits a ferromagnetic ordering below $T_c = 15.5$ K, with a magnetic moment of $1.25\,\mu_B$ at 2.5 K, perpendicular to the c-axis. The magnetic properties are analysed within the usual crystal field model; they are consistent with a doublet with mainly $|\pm 1/2\rangle$ character as the paramagnetic ground state.

1. INTRODUCTION

THE EQUIATOMIC RCuSi compounds (R = rare earth) crystallize in an hexagonal Ni_2In-type structure with space group $P6_3/mmc$ [1]. Crystallographic studies have been made first by Rieger and Parthé who proposed a hexagonal AlB_2-type structure [2], and more recently by Iandelli [1] and Mugnoli *et al.* [3] in order to confirm the ordered Ni_2In-type structure instead of the disordered AlB_2-type structure, even at room temperature.

Magnetic properties have been investigated on polycrystalline materials by susceptibility measurements for R = Ce to Ho [4, 5] and by neutron diffraction for R = Tb to Ho [6]. The results appeared first to be contradictory with regard to the type (ferro- or antiferromagnetic) of the existing interactions. Nevertheless, the actual interactions seem to be antiferromagnetic for the heavy rare-earths [6] and ferromagnetic for the light rare-earth [this work].

Here we report the results of resistivity (Section 2), neutron diffraction (Section 3) and magnetization (Section 4) experiments performed on polycrystalline samples of CeCuSi. The material was prepared by a direct fusion of the stoichiometric amount of the constituents in a cold crucible induction furnace. Annealing the sample at 750°C for 48 h strongly improved the X-ray powder patterns; in particular the superstructure lines of the Ni_2In-type structure with regard to the AlB_2-type structure are well defined after annealing, corresponding to a better alternate ordered arrangement of the Cu and Si atoms in 2(*c*) and 2(*d*) positions. The lattice parameters $a = 4.233$ Å, $c = 7.981$ Å were then obtained, in good agreement with the literature [1].

2. RESISTIVITY MEASUREMENTS

The resistivity of CeCuSi has been measured between 1.5 and 300 K (Fig. 1). It presents an anomaly at 15.5 K which may be attributed to the ferromagnetic ordering temperature T_c, according to the magnetic properties described below. This second-order phase transition is very well defined on the temperature derivative $d\rho/dT$ of the resistivity. In addition, a broad maximum is present on the $d\rho/dT$ curve around 36 K, which might be attributed to crystal field effects, at least partially. A comparison with the corresponding non magnetic compound LaCuSi would allow to clarify this point.

3. NEUTRON DIFFRACTION EXPERIMENT

Elastic neutron scattering experiments have been performed on the multidetector of the SILOE neutron reactor at the Centre d'Etudes Nucléaires in Grenoble. Two spectra were taken at 32 and 2.5 K with an incident neutron wavelength $\lambda = 2.498$ Å. The counting time was 6 h per spectrum.

The neutron diffraction pattern at 32 K (Fig. 2) is characteristic of the only nuclear scattering in an hexagonal system with space group $P6_3/mmc$ with $a = 4.228$ Å, $c = 7.926$ Å, this latter value being noticeably smaller than that measured at room temperature (see Section 1). Few additional lines are present, corresponding to around 10% of impurities. The calibrating factor was refined by a least square procedure on the nuclear intensities, using the Fermi lengths $b_{Ce} = 0.46$, $b_{Cu} = 0.79$ and $b_{Si} = 0.42 \times 10^{-12}$ cm. It is worth noting that a good agreement between observed and calculated intensities was obtained ($R_N = \Sigma|I_{obs} - I_{calc}|/\Sigma I_{obs} = 3.8\%$), in particular for reflections with odd-*l* indices, the intensities of which are directly related to the degree of ordering of Cu and Si atoms on the sites 2(*c*) and 2(*d*) [3, 6].

At low temperature, no additional lines appear in the neutron diffraction diagram as it can be seen in the difference diagram between low and high temperature patterns (Fig. 2). Only an increase of all the *l*-even nuclear reflections is observed. This is characteristic of a

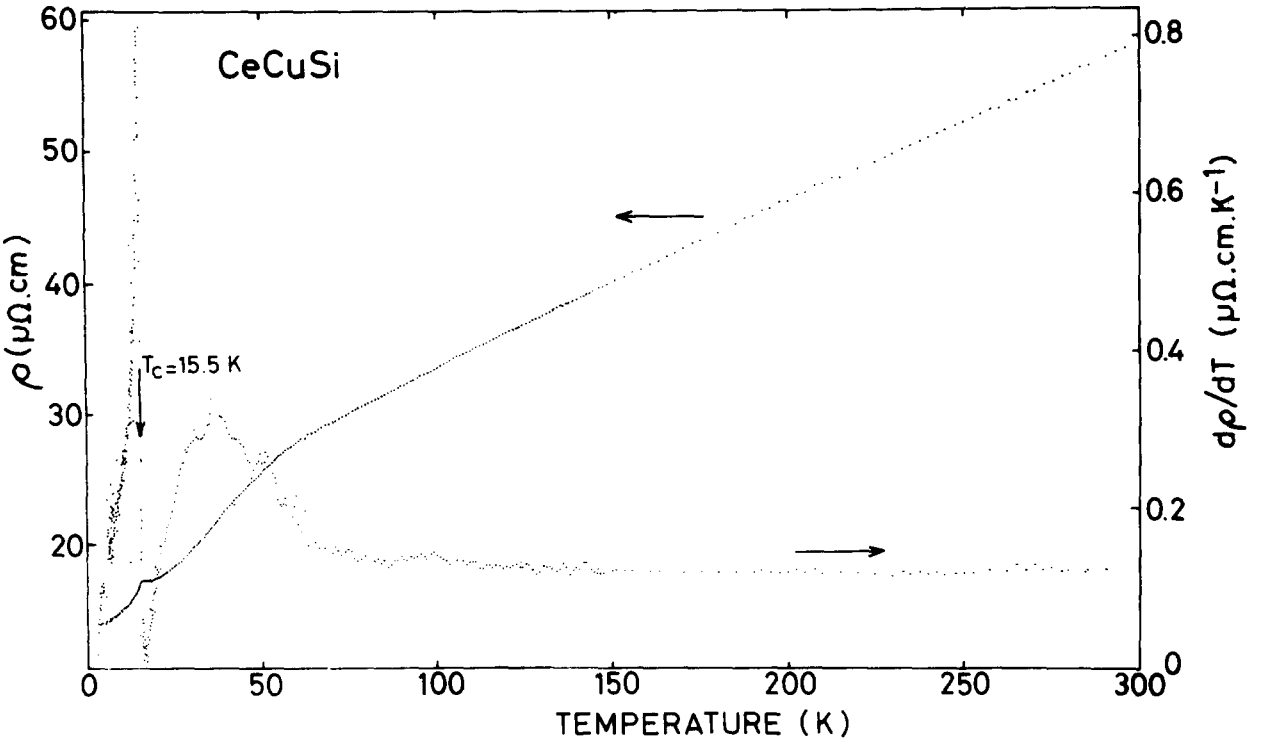

Fig. 1. Temperature dependence of the electrical resistivity (left scale) and its derivative (right scale) in CeCuSi.

collinear ferromagnetic ordering. The presence of magnetic contribution to the lines [0 0 2 l] indicates that the magnetic moments are not parallel to the c-axis. Taking into account the magnetic form factor of Ce^{3+} ion [7] the best agreement between observed and calculated intensities ($R_m = 18\%$) is obtained for a magnetic moment $M = 1.25\,\mu_B$ lying in the basal plane of the hexagonal unit cell. No further indication of the actual direction of the moments within this plane can be obtained from these data on polycrystalline material [8].

4. MAGNETIC PROPERTIES

Bulk magnetization measurements were performed on a polycrystalline sample by using the extraction method, in magnetic field up to 80 kOe and in the temperature range 1.5–300 K.

The temperature dependence of the reciprocal susceptibility follows a linear Curie–Weiss law above 90 K (see Fig. 3), leading to an effective paramagnetic moment $\mu_p = 2.54\,\mu_B$, a value very close to the free Ce^{3+} ion value, and a paramagnetic Curie temperature $\theta_p = -2$ K. At low temperature, the susceptibility deviates from the Curie–Weiss behaviour, and presents a huge increase at the ferromagnetic ordering temperature $T_c = 15.5$ K.

Several isothermal magnetization curves are reported in Fig. 4 in the low temperature region. Below $T_c = 15.5$ K, a ferromagnetic behaviour is observed, with a spontaneous magnetization of about $0.9\,\mu_B$/Ce at 1.5 K,

Table 1. Main crystallographic and magnetic data of CeCuSi

Crystal structure	Hexagonal, Ni_2In-type	
Space group	$P6_3/mmc$	
Lattice parameters	at 300 K	at 2.5 K
	$a = 4.233$ Å	$a = 4.228$ Å
	$c = 7.981$ Å	$c = 7.926$ Å
Curie temperature	$T_c = 15.5$ K	
Paramagnetic Curie Temperature	$\theta_p = -2$ K	(polycrystal)
Effective moment	$\mu_p = 2.54\,\mu_B$	
Ordered moment (at 2.5 K)	$M = 1.25\,\mu_B$	(⊥ c-axis)

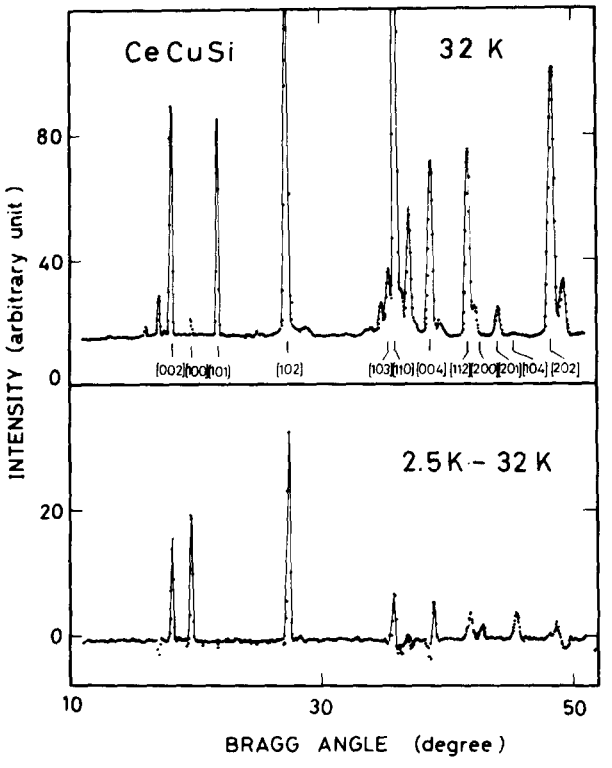

Fig. 2. Neutron diffraction patterns in CeCuSi. Upper part: diagram at 32 K; lower part: difference between diagrams at 2.5 and 32 K.

a value consistent with the neutron diffraction data, (see discussion in Section 5). Below 12 K and above 20 kOe, the magnetization increases slightly and linearly with the magnetic field, reaching for example 1.1 μ_B/Ce at 1.5 K in 80 kOe. This value is far from the saturated moment (2.14 μ_B), indicating strong crystal field effects (see below).

5. DISCUSSION

The main crystallographic and magnetic properties of CeCuSi are summarized in Table 1. Starting from all these data, a first analysis may be carried out with regard to the crystalline electric field (CEF). The $\bar{3}m$ point symmetry of the Ce^{3+} site in CeCuSi leads to a crystal field Hamiltonian which includes only second- and fourth-rank Stevens operators [9]:

$$\mathcal{H} = \alpha_J V_2^0 O_2^0 + \beta_J (V_4^0 O_4^0 + V_4^3 O_4^3),$$

where α_J and β_J are the Stevens coefficients. In this expression, the third term, V_4^3, is directly related to the degree of ordering of the Cu and Si atoms: it vanishes as soon as the distribution of these atoms is random on the sites 2(*c*) and 2(*d*).

A rough estimation of the V_l^m parameters may be performed within the oversimplified point charge model. This model generally gives a good order of magnitude for

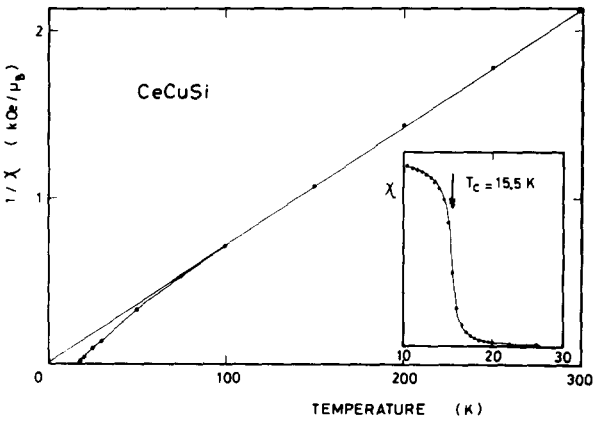

Fig. 3. Temperature dependence of the reciprocal susceptibility in CeCuSi. Inset: variation of the susceptibility at low temperature; T_c is the Curie temperature.

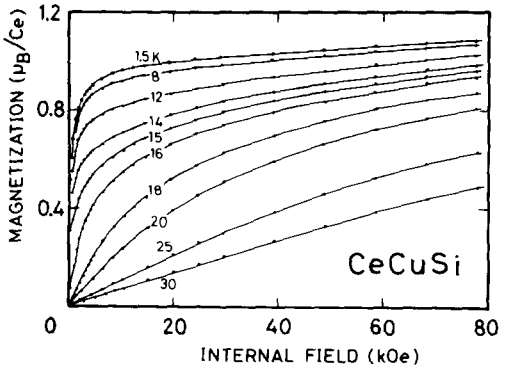

Fig. 4. Isothermal magnetization curves of CeCuSi (polycrystal) in the low temperature region.

the second-order CEF parameter, which is the preponderant term for determining the magnetic properties of these almost uniaxial systems. Taking a charge +3 on Ce, +1 on Cu and no charge on Si leads to the following parameters $V_2^0 = -160$ K, $V_4^0 = -5.5$ K and $V_4^3 = 1030$ K.

In these conditions, the multiplet $J = 5/2$ is split into three doublets which are mainly $|\pm M_J\rangle$ states ($M_J = 1/2$, 3/2 or 5/2), with a small mixing between $|\pm 1/2\rangle$ and $|\pm 5/2\rangle$ states due to the V_4^3 term. For the above parameters V_l^m, the ground state is found to be the doublet $|\pm 1/2\rangle$ in the paramagnetic state, well separated ($\Delta = 90$ K) from the first excited level $|\pm 3/2\rangle$, In the ordered state, the basal plane is then favoured as the easy magnetization plane, with an associated magnetic moment of 1.2 μ_B at 0 K, a value quite consistent with the neutron diffraction data. Note that the assumption of the doublet $|\pm 5/2\rangle$ as the ground state would lead, on the contrary, to an ordered magnetic moment close to the saturated value of 2.14 μ_B parallel to the c-axis.

On the other hand, the value of $1.25\,\mu_B$ for the ordered moment M perpendicular to the c-axis leads to a spontaneous magnetization of $3/4M$, i.e. $0.9\mu_B$, when measured on a polycrystal, considering a homogeneous distribution of the crystals inside the sample. This value is in good agreement with that observed experimentally (see Section 4).

In summary, the compound CeCuSi presents magnetic properties well described within a crystal field model involving the Ce^{3+} ion. The crystalline surrounding of the Ce^{3+} ions leads to a doublet with mainly $|\pm 1/2\rangle$ character as the paramagnetic ground state. Ferromagnetic interactions are present in CeCuSi, as in the neighbouring compound PrCuSi [4], giving rise to a ferromagnetic ordering below $T_c = 15.5$ K with an ordered magnetic moment of $1.25\,\mu_B$ at 2.5 K, perpendicular to the c-axis. Therefore, these results confirm the ferromagnetic tendency of the magnetic exchange interactions in the RCuSi compounds with light rare-earths, while the interaction are antiferromagnetic for the heavy rare-earths compounds [6]. From all the available data on CeCuSi, it appears that in this compound, the cerium ion does not exhibit any anomalous properties and behaves as a normal 3 + ion.

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