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Pressure effect on the magnetic and crystallographic structures in the $U(Ni_{1-x}Cu_x)_2Ge_2$ system

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Abstract

The pressure effect on the magnetic and crystallographic structures of the materials UCu_2Ge_2, and $U(Ni_{0.05}Cu_{0.95})_2Ge_2$ are studied by neutron diffraction in the applied pressure range of ambient to 0.63 GPa, at room temperature and 60 K. The compressibilities of the materials are found to be isotropic, and very similar for both materials and temperatures. This isotropy is explained by a free-electron gas control of the compressibility. No pressure effect on the magnetic structures or on the magnitude of the magnetic moments was observed for both materials. This result is discussed in the framework of the RKKY model. © 1998 Elsevier Science S.A.

Keywords: Pressure effect; Neutron diffraction; RKKY model

1. Introduction

Materials of the composition RM_2X_2, (R=U or lanthanides, M=3d transition metal, X=Si or Ge) usually crystallize in the tetragonal $ThCr_2Si_2$-type structure (space-group I4/mmm) [1]. These materials are paramagnetic at room temperature (RT) and undergo magnetic transitions to various ordered magnetic structures of the R sublattice at low temperatures (LT) [2,3]. Four distinctly different magnetic structures were found in $U(Ni_{1-x}Cu_x)_2Ge_2$ depending on x and on temperature (Fig. 1) [4]. These structures, AF-I, ferrimagnetic, AF-IA, and ferromagnetic, have different stacking of their ferromagnetic U planes along the c axis: (+ −), (+ + −), (+ + − −), and (+ +), respectively. In all four structures the magnetic moments are parallel to the c axis. As x is increased, the lattice parameters ratio, c/a, continuously increases (Fig. 2), while isothermal transformations between these magnetic structures occur (Fig. 1).

The magnetic interactions in materials of the composition RM_2X_2 are considered in terms of the isotropic RKKY model [5,6]. RKKY calculations show that the magnetic structure depends strongly on two parameters: the number of conduction electrons per magnetic atom (N), and the ratio of cell parameters (c/a) of the tetragonal cell

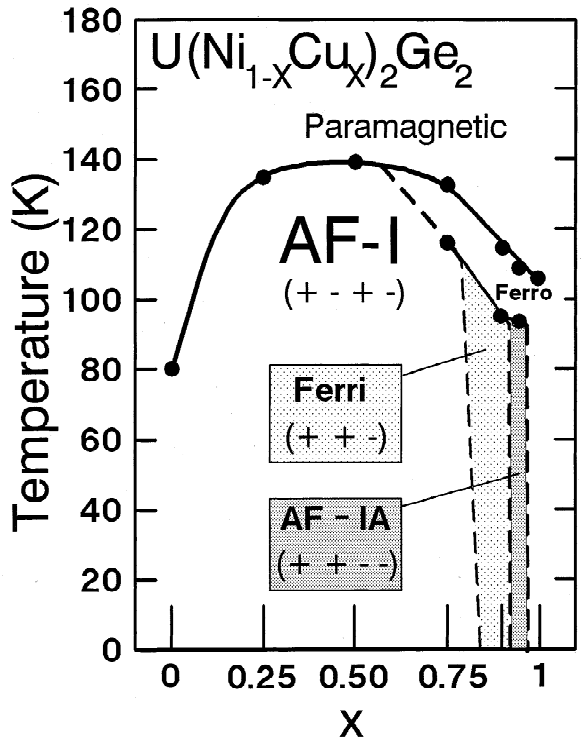

Fig. 1. Magnetic phase diagram (temperature vs. composition at zero applied magnetic field) of the $U(Cu_{1-x}Ni_x)_2Ge_2$ system (from [4]).

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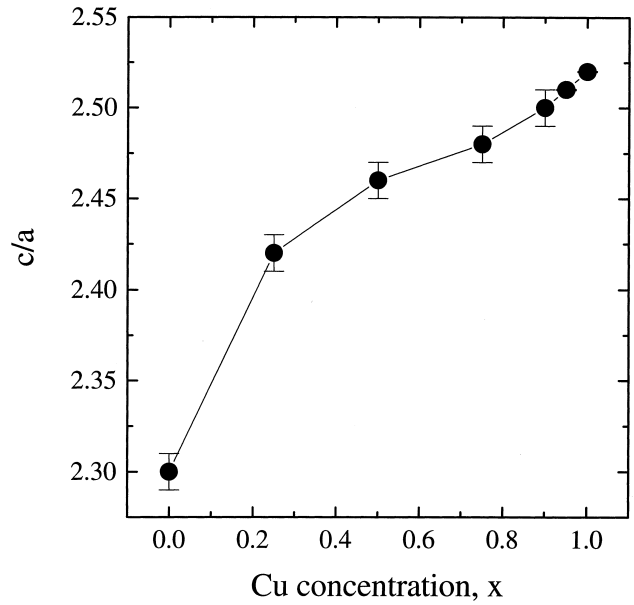

Fig. 2. The lattice parameters ratio, c/a, as a function of composition in the $U(Cu_{1-x}Ni_x)_2Ge_2$ compounds at RT. Data for $x=0$, 0.25, 0.5, 0.75, and 0.90 are taken from [4]. Error bars are smaller than the symbols unless displayed.

[5,6]. Thus, upon changing the c/a value, e.g. by the application of an external pressure, a change in magnetic structure is expected (in the framework of the RKKY model).

The present study of pressure effect on magnetic structures in $U(Ni_{1-x}Cu_x)_2Ge_2$ was therefore motivated by the idea that the magnetic structure can be modified by changing the lattice parameter ratio c/a. The samples we chose to study are at $x=0.95$ and 1, close to a magnetic phase change (Fig. 1), anticipating that the application of pressure will cause a change in c/a, large enough to drive a change in the magnetic structure.

2. Experimental details

We have used the samples prepared previously for neutron diffraction experiments at NRCN [4]. Time-of-flight neutron powder-diffraction data were collected on the Special Environment Powder Diffractometer (SEPD) [7] at Argonne's Intense Pulsed Neutron Source (IPNS). The SEPD was equipped with a helium pressure cell [8] mounted on a 12 W closed-cycle refrigerator (Displex). This apparatus allows the temperature of the sample to be controlled between 60 K and RT. The pressure cell design allows data collection between 0 and 0.63 GPa at a fixed scattering angle of $2\theta\sim\pm90°$. Four experiments, with $x=1$ at RT, $x=1$ at 60 K, $x=0.95$ at RT, and $x=0.95$ at 60 K, were performed at different pressures in the range of ambient to 0.63 GPa. The diffractograms were analyzed using the Rietveld technique with the GSAS program [9].

3. Results and analysis

The neutron diffraction results at RT and 60 K at ambient pressure are in agreement with previous studies for both compounds [4].

The RT neutron diffractograms of UCu_2Ge_2 and $U(Ni_{0.05}Cu_{0.95})_2Ge_2$ are consistent with the tetragonal

Table 1
Structural parameters of UCu_2Ge_2, as a function of pressure at RT. Rietveld refinements were done using the tetragonal space-group I4/mmm. Atom positions are U at 2a(0,0,0), Cu at 4d($0,\frac{1}{2},\frac{1}{4}$), and Ge at 4e(0,0,$z$). Structural parameters of the impurity phase, Cu_3Ge, were refined using the orthorhombic space-group Pmnm. Atom positions are: Cu at 2b($\frac{1}{4}$,0.246,$\frac{3}{4}$), Cu at 4f(0.496,0.246,$\frac{1}{4}$), and Ge at 2a($\frac{1}{4}$,0.783,$\frac{1}{4}$). B is the isotropic thermal displacement parameter. Numbers in parentheses represent standard deviations of the last significant digit. The weighted profile (R_{wp}) and expected (R_{exp}) agreement factors are also given [9]

P (GPa)		0	0.138	0.305	0.477	0.629
UCu_2Ge_2 (94 w/o)						
a (Å)		4.0576(2)	4.0558(2)	4.0539(2)	4.0519(2)	4.0496(2)
c (Å)		10.2285(5)	10.2240(5)	10.2195(5)	10.2147(5)	10.2090(2)
V (Å^3)		168.40(2)	168.18(2)	167.95(2)	167.70(2)	167.42(2)
B (Å^2)	U	0.27(5)	0.24(5)	0.27(5)	0.27(5)	0.24(5)
B (Å^2)	Cu	0.62(5)	0.61(5)	0.63(5)	0.60(5)	0.61(5)
B (Å^2)	Ge	0.59(5)	0.55(5)	0.55(5)	0.53(5)	0.54(5)
z	Ge	0.3805(2)	0.3805(2)	0.3804(2)	0.3803(2)	0.3803(2)
Cu_3Ge (6 w/o)						
a (Å)		5.227(1)	5.275(1)	5.272(1)	5.270(1)	5.267(2)
b (Å)		4.204(1)	4.202(1)	4.200(1)	4.198(1)	4.196(1)
c (Å)		4.578(1)	4.573(1)	4.576(1)	4.571(1)	4.569(1)
V (Å^3)		101.55(3)	101.38(3)	101.33(3)	101.14(3)	100.98(3)
R_{wp} (%)		13.0	12.1	11.6	11.2	11.4
R_{exp} (%)		4.4	4.3	4.2	4.1	5.2

Table 2
Structural parameters of $U(Ni_{0.05}Cu_{0.95})_2Ge_2$, as a function of pressure at RT. See caption of Table 1 for more information

P (GPa)		0	0.143	0.310	0.479
a (Å)		4.0590(1)	4.0572(1)	4.0553(1)	4.0532(1)
c (Å)		10.1923(2)	10.1883(2)	10.1831(2)	10.1785(2)
V (Å^3)		167.919(4)	167.709(4)	167.470(4)	167.215(4)
B (Å^2)	U	0.28(3)	0.28(3)	0.26(3)	0.26(3)
B (Å^2)	Cu	0.64(3)	0.62(3)	0.62(3)	0.61(3)
B (Å^2)	Ni	0.64(3)	0.62(3)	0.62(3)	0.61(3)
B (Å^2)	Ge	0.54(2)	0.55(2)	0.54(3)	0.54(3)
z	Ge	0.3797(1)	0.3797(1)	0.3797(1)	0.3798(1)
R_{wp} (%)		8.9	8.3	8.1	7.8
R_{exp} (%)		4.2	3.9	3.9	3.9

$ThCr_2Si_2$-type structure (space-group I4/mmm). The refined structural parameters (Table 1 and Table 2) are in agreement with previous measurements of both materials [4]. An impurity phase of Cu_3Ge was identified in the UCu_2Ge_2 sample, having a weight fraction of ~6% (Table 1).

The 60 K neutron diffractograms of UCu_2Ge_2 and $U(Ni_{0.05}Cu_{0.95})_2Ge_2$ are consistent with ferromagnetic and AF-IA structures (Fig. 1) of the U sublattice, respectively, in agreement with our previous results [4]. The U magnetic moments are $m_U=1.8(1)\ \mu_B$ and $m_U=1.82(4)\ \mu_B$, respectively, parallel to the tetragonal c axis.

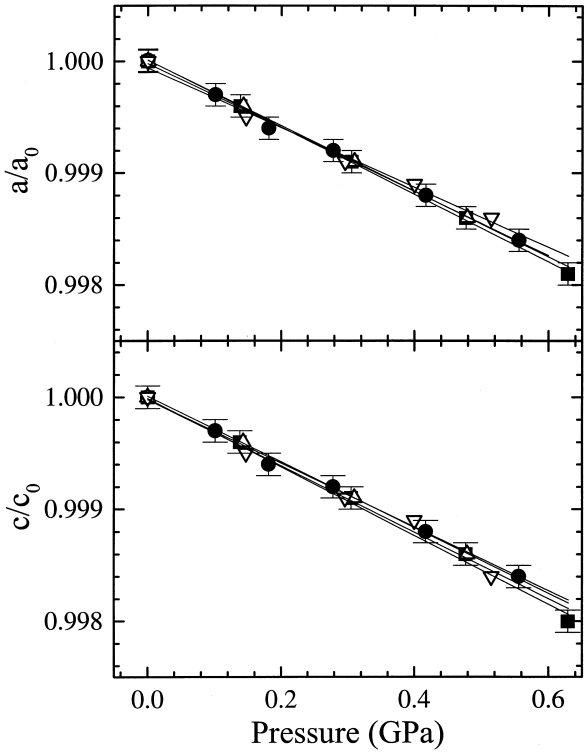

Fig. 3. The pressure dependence of the lattice parameters, normalized to their zero-pressure values. The different symbols represent different experiments as follows: (■) UCu_2Ge_2 at RT, (●) UCu_2Ge_2 at LT, (△) $U(Ni_{0.05}Cu_{0.95})_2Ge_2$ at RT, (▽) $U(Ni_{0.05}Cu_{0.95})_2Ge_2$ at LT. Error bars are smaller than the symbols unless displayed.

Table 3
RT and LT linear compressibilities, $k_{pq}=-[dq/dp]/q$ ($q=a,c$) (in 10^{-3} GPa^{-1}), for the UCu_2Ge_2 and $U(Ni_{0.05}Cu_{0.95})_2Ge_2$ materials, in the a and c directions, obtained from neutron diffraction data

Linear compressibilities	UCu_2Ge_2	$U(Ni_{0.05}Cu_{0.95})_2Ge_2$
k_{pa} (RT)	3.1(1)	2.93(3)
k_{pc} (RT)	3.1(1)	2.93(3)
k_{pa} (LT)	2.9(1)	2.7 (1)
k_{pc} (LT)	2.8(1)	3.0 (2)

There is a small, continuous and monotonic pressure effect on the crystallographic parameters (Table 1, Table 2 and Fig. 3), but no pressure effect on the magnetic structure or on the magnitude of the magnetic moment was observed.

Linear compressibilities $k_{pa}=-[da/dp]/a$, and $k_{pc}=-[dc/dp]/c$ at RT and 60 K are determined from these results (Table 3). The linear compressibilities were found to be isotropic, and very similar for both materials and temperatures (Table 3).

The linear coefficients of 'thermal expansion', $\alpha_a=[da/dT]/a$, and $\alpha_c=[dc/dT]/c$, are also obtained using the refined lattice parameters at RT and 60 K for both materials at ambient and high (~0.63 GPa) pressure (Table 4). It is found that in UCu_2Ge_2: $a\alpha_a \approx c\alpha_c$.

4. Discussion

The two materials were found to be quite soft, with an isotropic linear compressibility of $k_p=3.0(1)\times10^{-3}$ GPa^{-1} (Fig. 4; Table 3). This value lies between the linear compressibility of Cu (2.4×10^{-3} GPa^{-1}) and of Ag (3.3×10^{-3} GPa^{-1}) [10].

The linear compressibilities are found to be isotropic at pressures below 0.63 GPa, within the experimental uncertainty (Fig. 3; Table 3). This isotropy, found in crystallographically anisotropic (uniaxial) materials, can probably be explained by a free-electron gas control of the compressibility. This is a reasonable result for materials in which the magnetism is controlled by conduction electrons, i.e. the RKKY interactions.

Following the free-electron gas model in metals [11], a relation between the linear compressibility, k_p (in GPa^{-1}), and the number of conduction electrons per formula unit, Z, is given

$$Z = 0.006\frac{A}{\rho(k_p)^{3/5}} \quad (1)$$

where A is the molecular weight of the material (in g/mol), and ρ is the mass density of the material (in g/cm^3). The observed linear compressibility is $k_p=0.003$ GPa^{-1}, leading to $Z\sim10$ for both materials. This suggests a

Table 4
Ambient and high pressure linear 'thermal expansion' coefficients, $\alpha_q = [dq/dT]/q$ ($q = a,c$), for the UCu_2Ge_2, and $U(Ni_{0.05}Cu_{0.95})_2Ge_2$ materials, in the a and c directions, obtained from neutron diffraction data

Thermal expansion coefficient (10^{-6} K^{-1})	UCu_2Ge_2	$U(Ni_{0.05}Cu_{0.95})_2Ge_2$
α_a (ambient)	13.3(3)	12.3(1)
α_c (ambient)	5.7(6)	6.8(1)
α_a (0.63 GPa)	12.8(3)	11.9(1)
α_c (0.63 GPa)	4.9(6)	7.0(1)

contribution to the conduction band of ~2 electrons per Cu atom, and ~6 electrons per U atom, assuming no contribution from Ge electrons to the conduction band. This is consistent with the common valencies (i.e. 2 and 6) of Cu and U ions.

It can be seen (Fig. 4) that a 5% change in Cu concentration, x, results in an ~4‰ change in c/a, and a change of temperature (RT to LT) results in an ~2‰ change in c/a. However, because of the isotropic compressibility, the application of pressure leads to a negligible change in c/a. Thus, no change in the magnetic structure due to 0.63 GPa pressure is expected in the framework of the RKKY model, in agreement with the results of the present work.

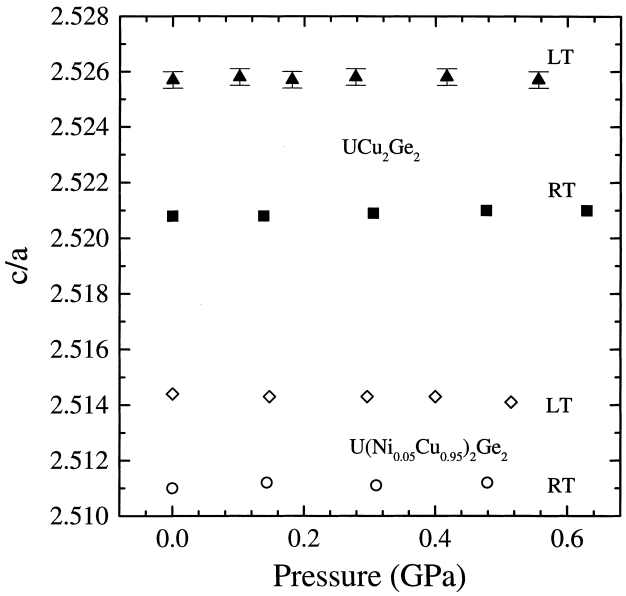

Fig. 4. The observed c/a as a function of pressure for the two materials at RT and LT. Error bars are smaller than the symbols unless displayed.

Using the isotropic compressibility, $k_{pa}/k_{pc} = 1$, and the relation between the linear coefficients of the thermal expansion, $a\alpha_a \approx c\alpha_c$ (valid for UCu_2Ge_2), one obtains: $\left(\frac{da/a}{dc/c}\right)_T = 1$ and $\left(\frac{da/a}{dc/c}\right)_P = \frac{c}{a}$ for the constant temperature and constant pressure experiments. We have no explanation for this result (at this stage). It may, however, indicate that the mechanisms controlling compressibility and thermal expansions are different.

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