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G.E. Grechnev¹, A.V. Logosha¹, A.S. Panfilov¹, I.V. Svechkarev¹,
O. Musil², P. Svoboda²

MAGNETOVOLUME EFFECT IN Ce(Ni_{1-x}Cu_x)₅ ALLOYS

¹B. Verkin Institute for Low Temperature Physics and Engineering
47 Lenin Ave., 61103 Kharkov, Ukraine

²Charles University, Faculty of Mathematics and Physics, DES
Ke Karlovu 5, 121 16 Prague 2, The Czech Republic
E-mail: panfilov@ilt.kharkov.ua

Magnetic susceptibility χ of the isostructural Ce(Ni_{1-x}Cu_x)₅ alloys ($0 \leq x \leq 0.9$) was studied as a function of the hydrostatic pressure up to 2 kbar at fixed temperatures of 77.3 and 300 K, using a pendulum-type magnetometer. A pronounced pressure effect on χ is found to be negative in sign and strongly (non-monotonously) dependent on the Cu content, showing a sharp maximum at $x \cong 0.4$. The experimental results are discussed in terms of the valence instability of Ce ion in the studied alloys. For the reference CeNi₅ compound the main contributions to χ and their volume dependence are calculated ab initio within the local spin density approximation (LSDA), and appeared to be in close agreement with experimental data.

Introduction

Many of Ce intermetallics are characterized by a strong hybridization of the magnetic 4*f* electrons with the conduction electron states resulted in delocalization of the 4*f* level and a change of its occupancy, and hence the Ce valence. As is evident from measurements of X-ray absorption and lattice parameters [1], together with the magnetic [2,3], electric and thermoelectric properties [3] in the isostructural Ce(Ni_{1-x}Cu_x)₅ alloys, the Ce valence decreases steadily from Ce⁴⁺ to Ce³⁺ with increase of the Cu content, and the system undergoes a series of transitions from the nonmagnetic metal with empty 4*f* level ($x = 0$) through the intermediate valence (IV) state combined with a nonmagnetic dense Kondo state ($0.1 \leq x \leq 0.8$) to the magnetic 4*f* metal ($0.9 \leq x \leq 1$). Thus, the reference CeNi₅ compound is the exchange-enhanced itinerant paramagnet [1,4,5] with the temperature dependent magnetic susceptibility exhibiting a broad maximum around 100 K, similar to those observed in YNi₅ and LuNi₅ [4,6]. On the other hand, the CeCu₅ compound is a Kondo lattice antiferromagnet with $T_N = 3.9$ K and $T_K = 2.2$ K [7]. The mag-

netic susceptibility in CeCu_5 at $T \geq 50$ K obeys a Curie–Weiss law with the effective magnetic moment value close to that expected for Ce^{3+} state [7–9]. Due to a direct relation between magnetic properties and the rare earth (RE) valence state, and also the strong correlation between the valence itself and RE ionic volume, the RE compounds with unstable f shell exhibit a large magnetovolume effect. Therefore, a study of pressure effect on magnetic properties of the systems with variable RE valence are of great interest to gain insight into a nature of the IV state.

Here we report results of our study of the pressure effect on the magnetic susceptibility of $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_5$ alloys in a wide range of Cu concentrations. The experimental results are supplemented by calculations of the magnetovolume effect value for the reference CeNi_5 compound, using a modified relativistic full potential linearized «muffin-tin» orbital method (FP-LMTO).

Experimental details and results

The polycrystalline samples of $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_5$ alloys ($0 \leq x \leq 4.5$) were prepared by arc-melting of a stoichiometric amount of initial elements in a water-cooled crucible under protective argon atmosphere. The study of X-ray powder diffraction at room temperature revealed that all samples crystallize in CaCu_5 -type

hexagonal structure, and obtained data on their lattice parameters agree closely with that published in literature. Any other phases were not detected within the resolution of the X-ray technique.

The pressure effect on magnetic susceptibility was measured under helium gas pressure up to 2 kbar at fixed temperatures, 77.3 and 300 K, using a pendulum magnetometer placed into the nonmagnetic pressure cell [10]. The relative errors of our measurements, performed in the magnetic field $H = 1.7$ T, did not exceed 0.05%. The pressure dependence $\chi(P)$ appeared to be linear in all samples studied. For each temperature, the values of χ at ambient pressure and their pressure derivatives, $d\ln\chi/dP$, were corrected for a weak field dependence of χ caused by ferromagnetic impurities. The corresponding corrections were less than 5%.

In Fig. 1 the typical pressure dependencies of the magnetic susceptibility for $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_5$ alloys demonstrate a mag-

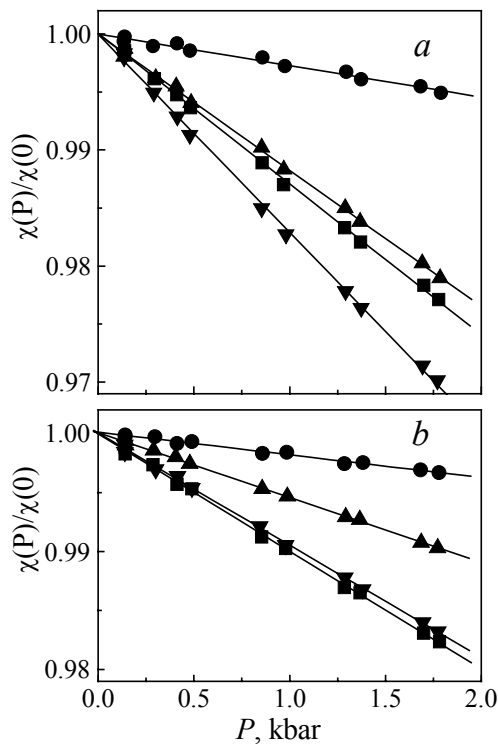


Fig. 1. Pressure dependence of the magnetic susceptibility of $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_5$ alloys at $T = 77.3$ (a) and 300 K (b), normalized to its value at $P = 0$: \bullet – $x = 0$, \blacksquare – 0.3, \blacktriangledown – 0.4, \blacktriangle – 0.5

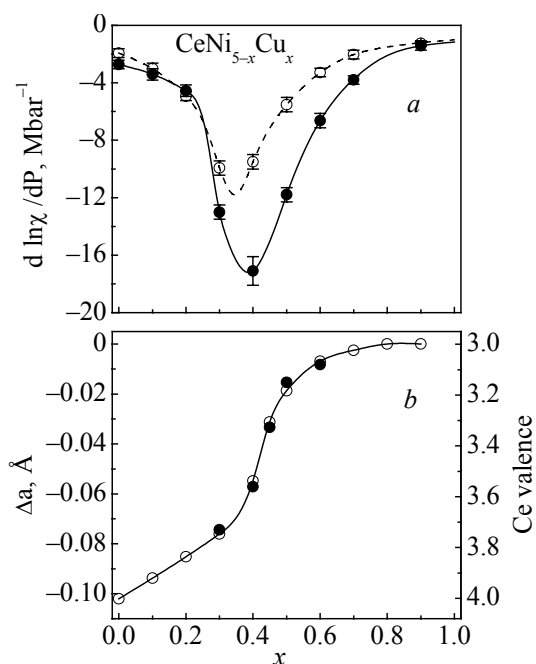


Fig. 2. (a) Pressure derivative of the magnetic susceptibility $d \ln \chi / dP$ in $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_5$ alloys at 77.3 K (\bullet) and 300 K (\circ). (b) Deviation of the a lattice parameter, Δa (\circ), in $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_5$ alloys from the $a(x)$ dependence for the Ce ion assumed to be in a trivalent state (left scale) and the Ce valence (\bullet) deduced from X-ray absorption studies (right scale) at room temperature versus Cu content x (according to the data of Ref. [1])

nitude of the pressure effect and its linear behavior. The negative sign of the effect is consistent with anticipation that high pressure has to increase the valence, since the Ce ion in the higher valence (less magnetic) state has a smaller volume.

Of particular interest is a strong and non-monotonous concentration dependence of the pressure effect which shows a sharp maximum in the vicinity of $x \approx 0.4$ for both temperatures, 77.3 and 300 K (Fig. 2,a). A comparison between the obtained experimental results and the data on concentration dependence of the lattice parameter a and the effective Ce valence v from [1] (Fig. 2,b) indicates that the maximum in $d \ln \chi(x, T) / dP$ correlates with a drastic change of a (and v) around $x \approx 0.4$ ($v \approx 3.5$).

It is interesting to note that a similar peculiarity in $d \ln \chi / dP$ versus valence was observed for various Yb compounds at room temperature [11]. As was shown, the relative change of χ with pressure is the most pronounced

also at the half-integer value of valence, $v = 2.5$, but contrary to Ce compounds, it has a positive sign, as can be expected.

Theory for CeNi_5

Ab initio calculations of the electronic structure were carried out for the reference compound CeNi_5 by employing a modified FP-LMTO method [12,13]. The exchange-correlation potential was treated in the LSDA approximation [14] of the density functional theory. To analyze the observed magnetovolume effect value in CeNi_5 , the magnetic susceptibility and its volume dependence were calculated within the modified method, wherein the external magnetic field H was taken into account by means of the Zeeman operator, $H(2s + 1)$. The latter was incorporated in FP-LMTO Hamiltonian [15] for calculations of the field-induced spin and orbital magnetic moments. The corresponding contributions to magnetic susceptibility were derived from the field-induced moments, which have been calculated in an external magnetic field of 10 T. The electronic structure calculations were performed for a number of lattice parameters close to the experimental one. The

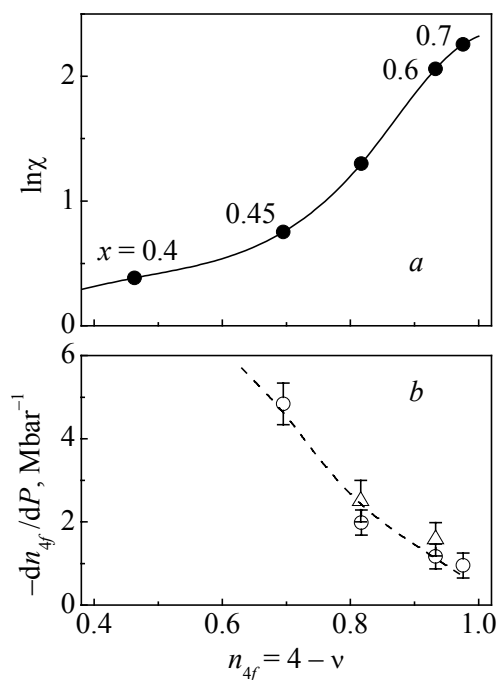


Fig. 3. Values of $\ln\chi$ at 77.3 K (a) and dn_{4f}/dP (b) both plotted against n_{4f} for $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_5$ alloys. Circles and triangles in (b) denote the data obtained with Eq. (1) and Eq. (4), respectively. Points for $x = 0.45$ are interpolation of the experimental data on concentration dependence of χ and $d\ln\chi/dP$

susceptibility, $d\ln\chi/d\ln V = 4.2$, is in agreement with that resulted from the experimentally observed pressure derivative for CeNi_5 at $T = 77.3$ K, $d\ln\chi/d\ln V = 3.9 \pm 0.4$. Thus, it has been demonstrated that LSDA provides an adequate description of the strongly exchange enhanced magnetic susceptibility of CeNi_5 and its pressure dependence.

Discussion

As is shown, the LSDA allows to describe the magnetovolume effect in the reference CeNi_5 compound that gives grounds for future application of LSDA *ab initio* approaches to some $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_5$ alloys. Here, however, we shall restrict our consideration of the experimental data in alloys within a phenomenological approach.

A. Concentration dependence

Anticipating the pressure effect on the magnetic susceptibility to arise mainly from the change of Ce valence, or the fractional occupation of the $4f^1$ magnetic state n_{4f} ($v = 4 - n_{4f}$), the pressure effect can be analyzed within a simple relation

equilibrium lattice spacing a and corresponding theoretical bulk modulus B were determined from the dependence of the total energy on the unit cell volume (the ratio c/a was fixed at its experimental value), and appeared to be $a = 8.96$ a.u. and $B = 1.9$ Mbar (to be compared with experimental $a = 9.2$ a.u. [1] and $B = 1.43$ Mbar [16]). The differences between theory and experiment on bulk properties of CeNi_5 are presumably related to the overbonding tendency of the LSDA approach [12].

The strongly volume dependent spin contribution to χ originates predominantly from the $3d$ states of Ni. Regarding the orbital contribution to χ , it comes mainly from electrons in atomic sphere of Ce and amounts to about 20% of total susceptibility. At the theoretical lattice parameter, the calculated total susceptibility at $T = 0$ K ($2.9 \cdot 10^{-3}$ emu/mol) appeared to be very close to the experimental one ($3.0 \cdot 10^{-3}$ emu/mol [4]). The corresponding volume derivative of sus-

$$\frac{d \ln \chi}{dP} \approx \frac{\partial \ln \chi}{\partial n_{4f}} \frac{dn_{4f}}{dP} \quad (1)$$

in terms of the pressure dependence of n_{4f} (or ν). The most reliable results of such analysis would be expected in the Cu-rich alloys at low temperatures where the $4f$ contribution χ_{4f} becomes dominant.

In Fig. 3,*a* the χ versus n_{4f} dependence is shown for $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_5$ alloys ($0.4 \leq x \leq 1$) at 77.3 K, which is obtained by using the experimental $\chi(x)$ values and $\nu(x)$ data of Fig. 2,*b*. A substitution of the resulted from Fig. 3,*a* derivatives $\partial \ln \chi / \partial n_{4f}$ and experimental data on $d \ln \chi / d \ln P$ at 77.3 K into Eq. (1) gives dn_{4f} / dP value which strongly depends on n_{4f} (Fig. 3,*b*). As is seen, the maximum value of dn_{4f} / dP is expected at $n_{4f} = 0.5$ ($\nu = 3.5$) to be about $-6.5 \pm 1.5 \text{ Mbar}^{-1}$. The corresponding estimates of the valence change under pressure, $dv/dP = -dn_{4f}/dP$, are of the same order as those resulted from the study of magnetovolume effect in SmB_6 (2 Mbar^{-1} [17]) and from the measurements of resonant inelastic X-ray emission in YbAl_2 under pressure ($\sim 5 \text{ Mbar}^{-1}$ [18]).

B. Temperature dependence

In a simple empirical model which includes interconfiguration fluctuations between f^{n+1} and f^n levels [19], the contribution of the $4f^0$ ($J = 0$) and $4f^1$ ($J = 5/2$) states of Ce to magnetic susceptibility is given by

$$\chi_{4f}(T) = N\mu^2 n_{4f}(T) / 3k(T + T_f). \quad (2)$$

Here N is the Avogadro number, μ – effective magnetic moment of the $4f^1$ state, T_f – the characteristic temperature (valence fluctuation temperature, or Kondo temperature, or heavy-fermion bandwidth). It should be mentioned that a quantitative analysis of the $\chi_{4f}(T)$ dependence using Eq. (2) requires the complete data on $n_{4f}(T)$ (and probably on $T_f(T)$ as well) which are actually unavailable. Furthermore, to separate the $\chi_{4f}(T)$ term from the experimental data on $\chi(T)$ one needs to know a background contribution χ_0 , which generally can not be neglected.

A simplified analysis of the experimental data can be performed assuming n_{4f} , T_f and χ_0 to be temperature independent. Then the magnetic susceptibility obeys a modified Curie–Weiss law,

$$\chi(T) = \chi_0 + \chi_{4f}(T) \equiv \chi_0 + C / (T - \theta), \quad (3)$$

with $C = N\mu^2 n_{4f} / 3k$ and $\theta = -T_f$. For the representative $\text{Ce}(\text{Ni}_{0.5}\text{Cu}_{0.5})_5$ alloy, the best fit of Eq. (3) to the experimental data at $T \geq 50$ K (Fig. 4,*a*) [2] is obtained with $\chi_0 = 0.6 \cdot 10^{-3} \text{ emu/mol}$, $C = 0.48 \text{ K} \cdot \text{emu/mol}$ and $\theta = -79 \text{ K}$. It should be pointed out that the estimate $n_{4f} = 0.6$, resulted from C , is in a reasonable agreement with the value of 0.8 that follows from the data in Fig. 2,*b* for $x = 0.5$.

As is evident from Eqs. (2) and (3), the pressure effect on the $4f$ susceptibility is governed by changes of n_{4f} and T_f with pressure, as

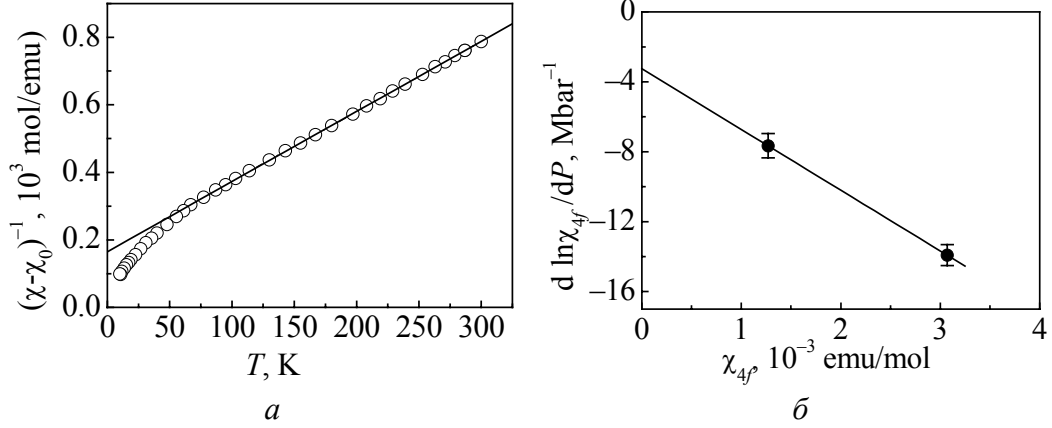


Fig. 4. Temperature dependence of the magnetic susceptibility χ (a) and pressure derivative $d \ln \chi_{4f} / dP$ plotted against χ_{4f} (b) for $\text{Ce}(\text{Ni}_{0.5}\text{Cu}_{0.5})_5$ alloy

$$\frac{d \ln \chi_{4f}(T)}{dP} = \frac{d \ln C}{dP} - \frac{1}{T + T_f} \frac{dT_f}{dP} \equiv \frac{d \ln n_{4f}}{dP} - \frac{\chi_{4f}(T)}{C} \frac{dT_f}{dP}, \quad (4)$$

being a linear function of $1/(T + T_f)$ or $\chi_{4f}(T)$. The data on $d \ln \chi_{4f} / dP$ for $\text{Ce}(\text{Ni}_{0.5}\text{Cu}_{0.5})_5$ alloy were derived from the measured effect, $d \ln \chi / dP$, in the framework of Eq. (3) using a value $d \ln \chi_0 / dP \sim -1 \text{ Mbar}^{-1}$ as a rough estimate for the pressure dependence of the background [20] which is assumed to originate from $3d(4d)$ itinerant electrons. The obtained values $d \ln \chi_{4f} / dP$ are plotted in Fig. 4,b as a function of $\chi_{4f}(T)$. Its linear approximation in accordance with Eq. (4) gives

$$\frac{d \ln C}{dP} = \frac{d \ln n_{4f}}{dP} = -3.2 \pm 0.7 \text{ Mbar}^{-1}, \quad \frac{dT_f}{dP} = 1650 \pm 250 \text{ K} \cdot \text{Mbar}^{-1}.$$

The resultant value $dn_{4f}/dP = -2.5 \pm 0.5 \text{ Mbar}^{-1}$ is in line with the value $dn_{4f}/dP = -2.0 \pm 0.3 \text{ Mbar}^{-1}$ obtained previously for $x = 0.5$ from analysis of the concentration dependence of the pressure effect within Eq. (1). From the pressure dependence of T_f the corresponding Grüneisen parameter, Ω , is estimated as

$$\Omega \equiv -\frac{d \ln T_f}{d \ln V} = B \frac{dT_f}{dP} = 31 \pm 5 \quad (5)$$

using the experimental bulk modulus $B = 1.5 \text{ Mbar}$ [21]. The Anderson impurity model provides the Kondo temperature and its pressure derivative to be described in terms of n_{4f} [22]:

$$T_K \propto \frac{1 - n_{4f}}{n_{4f}}, \quad \frac{d \ln T_K}{dP} = \frac{1}{1 - n_{4f}} \frac{d \ln n_{4f}}{dP}. \quad (6)$$

Then, assuming $T_f \propto T_K$ and using in Eq. (6) the values $dn_{4f}/dP = -3.2 \pm 0.7$ Mbar⁻¹ and $n_{4f} = 0.8$ evaluated above for the alloy with $x = 0.5$, one obtains

$$\Omega_f = \Omega_K = -\frac{d \ln T_K}{d \ln V} = 24 \pm 5, \quad (7)$$

in reasonable agreement with the direct estimate (5).

For Ce(Ni_{0.4}Cu_{0.6})₅ alloy, the analogous analysis in the framework of Eq. (3) and Eq. (4) yields the following Curie–Weiss parameters: $C \sim 0.806$ K·emu/mol, $\chi_0 \sim 0$, $T_f = -\theta = 26$ K, and their pressure derivatives:

$$\frac{d \ln C}{dP} = \frac{d \ln n_{4f}}{dP} = -1.7 \pm 0.5 \text{ Mbar}^{-1}, \quad \frac{dT_f}{dP} = 620 \pm 100 \text{ K} \cdot \text{Mbar}^{-1}.$$

The latter results in the Grüneisen parameter $\Omega_f = 35 \pm 6$, assuming the bulk modulus value $B = 1.5$ Mbar, as in the Ce(Ni_{0.5}Cu_{0.5})₅ alloy. The similar estimate follows from Eqs. (6) and (7) with $n_{4f} = 0.93$ derived from the data in Fig. 2, *b*. The reasonable description of the Grüneisen parameter for alloys with $x = 0.5$ and 0.6 with Anderson model [21] allows to consider the Cu-rich alloys studied in the present work as the nonmagnetic Kondo lattices.

Conclusions

The pressure effect on magnetic susceptibility of Ce(Ni_{1-x}Cu_x)₅ alloys has been observed for the first time. This effect is negative in sign, and also strongly and non-monotonously dependent on the Cu content. For the reference CeNi₅ compound, the pressure effect value is successfully described within LSDA approximation, using the modified full potential relativistic FP-LMTO method. For Ce(Ni_{1-x}Cu_x)₅ alloys the effects of pressure and alloying on the valence state of Ce ion are the most pronounced around $x \sim 0.4$, which corresponds to the half-integer valence $\nu \sim 3.5$. In other words, the fractional occupation $n_{4f} \sim 0.5$ with the nearly degenerate f^0 and f^1 configurations of electronic states is favorable for the valence instability. It is also found that the main contributions to the pressure effect on magnetic susceptibility for the Cu-rich alloys are i) the decrease of the effective Curie constant and ii) the increase of the characteristic temperature T_f . The latter exhibits a large and positive value of the Grüneisen parameter, which can be apparently described within the Anderson impurity model. Both of these contributions have their origin in the change of the Ce valence state caused by depopulation of the f state under pressure due to its shift relative to the Fermi energy.

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