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STUDY OF STRUCTURAL TRANSFORMATIONS OF EQUIATOMIC COMPOUNDS OF RARE EARTH METALS WITH COPPER

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Electrical resistivity, magnetic susceptibility, X-ray diffraction and differential thermal analysis have been performed over a wide temperature range on binary compounds RCu. Melting points or decomposition temperatures for RCu (R = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy) phases and a number of FeB–CsCl structural transitions are reported, and heats and entropies of transformation are evaluated. Large hysteresis effects are observed for the structural transformations at different temperatures.

In LaCu and CeCu no structural transformation was detected, while TbCu and DyCu failed to reveal any high-temperature thermal effect of transformation. In EuCu a non-reproducible thermal effect was evidenced after thermal cycling.

It has been reported that the majority of equiatomic compounds formed by rare earths (R) crystallize with the CsCl, CrB or FeB structures [1]. In the RCu series, the compounds formed by the lighter rare earths show the orthorhombic FeB structure ($_oP8$ in Pearson's notation) stable at room temperature, while the heavier rare earths form RCu cubic phases of CsCl type ($_cP2$). SmCu is the first cubic compound at 298 K.

The equilibrium phase diagrams have been determined for the majority of R–Cu in this laboratory [2, 3]. Study of the Nd–Cu diagram [4] has evidenced a structural transition for the equiatomic compound (Fig. 1). Both magnetic and structural transitions have already been detected for other 1:1 compounds formed by heavy rare earths and Y with copper [5–9].

The CsCl-type compounds RCu [10] and RAg [11] are antiferromagnetic, while RZn [12, 13], RCd [14, 15] (except PrCd and YbCd) and TbHg [14] are ferromagnetic. The experimental results have been explained in terms of RKKY exchange interaction, due to the polarization of conduction electrons. The compounds of the light R were also understood on the same basis, introducing new types of magnetic ordering, such as the screw structure.

In this paper we report calorimetric and structural results obtained during a study of the phase transitions of RCu compounds. In order to obtain further evidence of

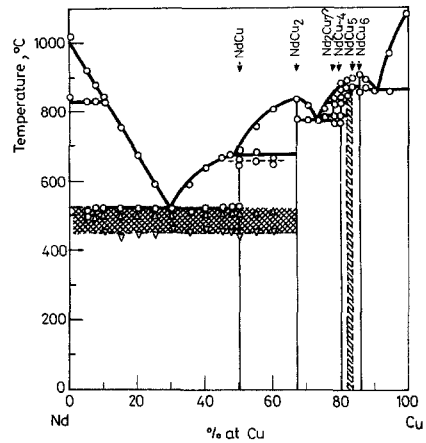

Fig. 1 The Nd–Cu phase diagram, where the hysteresis in the structural transformation of NdCu is evidenced

the presence of thermal hysteresis in some RCu phases, resistivity results for NdCu are also reported.

Experimental

R metals (Rare Earths Products Inc.; 3N), except Eu (Michigan Chem. Co.; 2N), and copper (Koch-Light; 5N) were used as starting materials. The samples (each consisting of 1 g of a stoichiometric mixture of the elements) were sealed in molybdenum crucibles under pure argon and were melted a number of times in an induction furnace while being carefully shaken to ensure homogeneity.

Differential thermal analysis (DTA) was performed during both heating and cooling, as described previously [16]. The samples were thermally cycled to check the reproducibility of the data. In some cases, additional thermal treatments were applied.

The alloys were homogeneous on micrographic analysis and were grey metallic coloured. They oxidized easily in air and were brittle.

Resistivity tests were performed by the conventional four-wire technique, in which the wires were spot-welded on the samples.

The crystal structures of the phases were checked by the X-ray powder method. High-temperature measurements of reticular parameters were carried out using a Rigaku-Denki high-temperature powder chamber.

The values of ΔH were determined following a procedure well established in this laboratory [17]. The mean value of three measurements is reported in Table 1; the accuracy is expected to be ±10%.

Table 1 Crystallographic, thermal and thermodynamic properties of RCu phases

Comp.	Struct., 298 K	T_m., K±5K	$T_{tr.}$, K±5K heat.	cool.	$P_{tr.}$, GPa 298 K	$\Delta H_{tr.}$, kJ/mol	$\Delta S_{tr.}$, J/mol K	Ref.
LaCu	FeB	798 p						2
CeCu	FeB	778 p						2
PrCu	FeB	853 p	723	720		2.1	2.9	t.w., 2
NdCu	FeB	943 p	783	703		1.7	2.1	t.w., 4
SmCu	CsCl	1013 p	633	315	0.5	1.7	2.5	t.w., 2
EuCu	FeB	805 p	n.r.					t.w., 3
GdCu	CsCl	1103 m	553	240		1.9	3.3	2,6
TbCu	CsCl	1173 m		116				t.w., 2,7
DyCu	CsCl	1228 m		63				2,7
HoCu	CsCl	1280 m						t.w., 2
ErCu	CsCl	1328 m		13				2,8

p = peritectic decomposition, m = congruent melting, n.r. = not reproducible

Results

The results obtained in the present work are summarized in Table 1, together with literature data.

For SmCu, two structures (CsCl and FeB type) are reported in the literature [2]; the FeB structure is probably stabilized at room temperature by impurities. It must be noted that the higher-temperature modification, which is more symmetric (CsCl), is denser. This phenomenon, although opposite to the normal behaviour of the metallic phases (where the high-temperature phase is less compact), has been found in other series of intermetallic compounds of the rare earths, such as RAu [18].

The volume contraction in the transition to the high-temperature phase can account for the sudden decrease in the resistivity of NdCu (Fig. 2) observed in correspondence with the transition temperature, in accord with the behaviour for most metals where a decrease in resistivity follows the volume contraction obtained under pressure. The constant slope of ρ *vs.* T indicates that the conduction electrons do not play an important role in the transformation.

The $\Delta S_{tr.}$ values are found to be practically independent of the different R and very near to the value obtained in the allotropic transitions of rare earths [19]. However, in this case the entropy difference is justified on the basis of the volume variation by the formula $dS/dV = \gamma C_v/V$, where γ lies between 1 and 3 (but generally $\gamma \cong 2$) and $C_v \cong 3E$ [20]. For the compounds RCu, this contribution is negative: $\Delta S = 1.0$ J mol^{-1} K^{-1}. If we use thermal expansion available for GdCu [6, 21] and assume that they are of the same order of magnitude for the other compounds, we obtain $V_{H.T.} \cong 98\ V_{L.T.}$. As the mean value of ΔS is about 2.7 J/mol · K for all the examined compounds, $\Delta S \cong 3.7$ J/Km is due to the magnetic ordering, and changes in the bonds and in the coordination of the atoms.

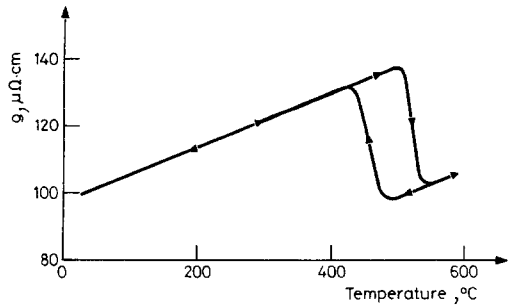

Fig. 2 Thermal dependence of resistivity of NdCu

The two structural types FeB and CsCl are sketched in Fig. 3. The FeB type is characterized by "trigonal prisms" of *R* and zig-zag chains of Cu in contact, while in the cubic cell Cu atoms are insulated from each other and are bonded only to *R* atoms.

Since the high-temperature phase is more contracted than the low-temperature one, it ought to be possible to obtain the transition at a lower temperature, by applying the appropriate pressure to the compounds. From the Clausius–Clapeyron relation we obtain, with the above approximation, $\Delta P/\Delta T = \Delta S/\Delta V = -5$ MPa/K. At present we have effectively obtained such a transition in SmCu under 0.5 GPa of pressure.

The characteristic temperatures for different compounds are reported in Fig. 4 *vs.* the atomic number of the trivalent rare earth.

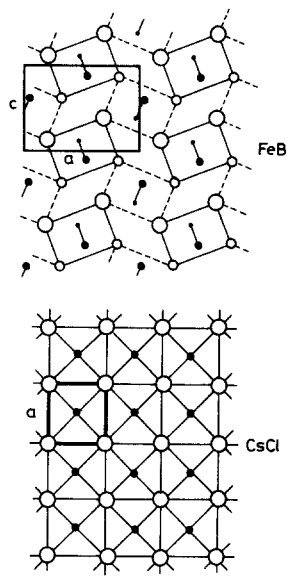

Fig. 3 Lattice deformation in the structural transformation FeB–CsCl

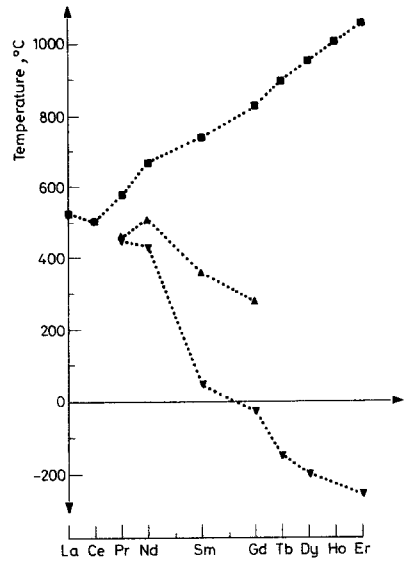

Fig. 4 Characteristic temperatures of RCu phases formed by trivalent rare earths. ■ decomposition or melting point, ▲ transformation temperature (heating), ▼ transformation temperature (cooling)

Conclusion

We have confirmed the presence of thermal hysteresis in the transformations of equiatomic RCu compounds. The thermal effects on heating were evaluated and the obtained $\Delta S_{tr.}$ values were found similar to those reported in the literature for the allotropic transitions of rare earth metals [22].

The observation by Rao [23] that thermal hysteresis in transformations is found when there is a large difference in the molar volumes of the phases, is confirmed in the present case.

In the RCu transitions the ΔS values were found to be due to the changes in the phase volume, the bonds and the magnetic ordering.

As the high-temperature phase is denser than the low-temperature one, we are continuing investigations on RCu phases by means of structural measurements under pressure, while studying the thermal, structural and magnetic properties of TbCu and DyCu, to ascertain if the low-temperature transformation is exclusively of magnetic origin.

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References

1 A. Iandelli and A. Palenzona, Handbook of the Physics and Chemistry of Rare Earths, K. A. Gschneidner Jr. and E. Eyring Eds., North-Holland, Amsterdam, 1979, vol. 2, p. 1.
2 M. M. Carnasciali, G. A. Costa and E. A. Franceschi, Gazz. Chim. Ital., 113 (1983) 239.
3 G. A. Costa, E. A. Franceschi and A. Tawansi, J. Less-Common Met., in press.
4 M. M. Carnasciali, G. A. Costa and E. A. Franceschi, J. Less-Common Met., 92 (1983) 97.
5 P. Morin and J. Laforest, Comptes Rendus Acad. Sci., B277 (1973) 353.
6 J. C. M. Van Dongen, T. T. M. Palstra, A. F. J. Morgownik, J. A. Mydosh, B. M. Geerken and K. H. J. Buschow, Phys. Rev., B27 (1983) 1887.
7 P. Morin and J. Pierre, Phys. Stat. Sol., A21 (1974) 161.
8 R. E. Walline and W. E. Wallace, J. Chem. Phys., 42 (1965) 604.
9 H. Balster, H. Ihrig, A. Kockel and S. Methfessel, Z. Physik, B21 (1975) 241.
10 J. W. Cable, W. C. Koehler and H. C. Child, J. Appl. Phys., 36 (1975) 1096.
11 R. E. Walline and W. E. Wallace, J. Chem. Phys., 41 (1964) 3285.
12 G. T. Alfieri, E. Banks and K. Kanematsu, J. Appl. Phys., 37 (1966) 1254.
13 P. Morin, J. Rouchy and E. du Tremolet de Lacheisserie, Phys. Rev., B16 (1977) 3182.
14 G. T. Alfieri, E. Banks, K. Kanematsu and T. Ohoyama, J. Phys. Soc. Japan, 23 (1967) 507.
15 A. M. Stewart, G. A. Costa and G. L. Olcese, Australian J. Phys., 27 (1974) 383.
16 E. Franceschi, J. Less-Common Met., 87 (1982) 249.
17 A. Palenzona, Thermochim. Acta, 5 (1973) 473.
18 O. D. McMasters, K. A. Gschneidner Jr., G. Bruzzone and A. Palenzona, J. Less-Common Met., 25 (1971) 135.
19 H. K. King, Bulletin of Alloy Phase Diagrams, 3 (1982) 276.
20 J. C. Slater, Introduzione alla Chimica Fisica, Sansoni Ed., Firenze, 1949, p. 239.
21 Y. Gefen and M. Rosen, Scripta Metallurgica, 14 (1980) 645.
22 K. A. Gschneidner, J. Less-Common Met., 43 (1975) 179.
23 C. N. R. Rao and K. J. Rao, Phase transitions in solids, McGraw-Hill Inc., Chatham, 1978, p. 34.

Zusammenfassung — Messungen der elektrischen Leitfähigkeit und der magnetischen Susceptibilität sowie röntgendiffraktometrische und differentialthermoanalytische Untersuchungen von binären Verbindungen des Typs RCu wurden in einem weiten Temperaturbereich ausgeführt. Schmelzpunkte bzw. Zersetzungstemperaturen von RCu-Phasen (R = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb und Dy) und eine anzahl von Phasenübergängen im System FeB—CsCl sind zusammen mit den bestimmten Entropiewerten der Phasenübergänge angegeben. Die Temperaturabhängigkeit der Phasenübergänge weist eine ausgeprägte Hysterese auf. In den Systemen LaCu und CeCu konnten keine Phasenübergänge festgestellt werden, während sich bei TbCu und DyCu kein auf einen Phasenübergang hinweisender thermischer Effekt im Hochtemperaturbereich zeigt. Bei EuCu wurde ein nicht-reproduzierbarer thermischer Effekt nach einem thermischen Kreisprozeß nachgewiesen.

Резюме — Измерения электрического удельного сопротивления, магнитной воспроиимчивости, дифракция рентгеновских лучей и дифференциальный термический анализ были использованы для изучения в широкой области температур двойных соединений RCu. Для соединений RCu (R = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb и Dy) приведены точки плавления или температуры разложения, отдельные фазы и ряд структурных переходов типа FeB—CsCl, а также определены теплоты энтропий этих превращений. Для структурных пере-

ходов при различных температурах наблюдались большие гистерезисные эффекты. Для соединений LaCu и CeCu не было обнаружено структурного превращения, тогда как для соединений TbCu и DyCu не представилось возможным обнаружить какой-либо высокотемпературный термический эффект превращения. Для соединения EuCu после циклического термического нагрева был обнаружен невоспроизводимый термический эффект.