The vibrational and configurational entropy of α-brass ☆

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A B S T R A C T

The heat capacities of two samples of a fcc Cu–Zn alloy with the composition CuZn15 and CuZn34 were measured from $T = 5$ K to 573 K using relaxation and differential scanning calorimetry. Below $\sim$90 K, they are characterised by negative excess heat capacities deviating from ideal mixing by up to -0.20 and -0.44 J $\cdot$ mol^{-1} $\cdot$ K^{-1} for CuZn15 and CuZn34, respectively. The excess heat capacities produce excess vibrational entropies, which are less negative compared to the excess entropy available from the literature. Since the literature entropy data contain both, the configurational and the vibrational part of the entropy, the difference is attributed to the excess configurational entropy. The thermodynamics of different short-range ordered samples was also investigated. The extent of the short-range order had no influence on the heat capacity below $T = 300$ K. Above $T = 300$ K, where the ordering changed during the measurement, the heat capacity depended strongly on the thermal history of the samples. From these data, the heat and entropy of ordering was calculated. The results on the vibrational entropy of this study were also used to test a relationship for estimating the excess vibrational entropy of mixing.

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1. Introduction

The thermodynamics of copper-zinc alloys (brass) was subject of numerous investigations. Brass is characterised by an excess enthalpy and excess entropy of mixing, both of which are negative. The enthalpic data were measured by solution calorimetry e.g., [1–3] and based on chemical potential data calculated from phase equilibrium experiments e.g., [4–6], the excess entropy of mixing could be evaluated e.g., [7–9]. This excess entropy contains both, the vibrational and the configurational parts. The excess vibrational entropy, defined as the deviation from the entropy of a mechanical mixture of the end members A and B (i.e., $S_m^{mechmix} = X_A S_m^A + X_B S_m^B$), can be determined by measuring the low temperature heat capacity (5 to 300 K) versus composition behaviour. The determination of the excess configurational entropy, i.e., the excess entropy coming from non-random atomic distributions and defects, is much more difficult. Here, neutron scattering investigations together with computer simulations are normally used. If, however, reliable data of the total excess entropy (from enthalpic and chemical potential data) are available, the measurement of the excess vibrational entropy enables the determination of the excess configurational entropy simply by subtraction. Since configurational and vibrational entropies may have

different temperature dependencies, it is worthwhile to separate the entropic effects. This is one aim of this study. Another aim is to deliver experimental data so that first principles studies can test their models on a disordered alloy, whose structural details (short-range order) depend on temperature.

Cu–Zn alloys in the Cu-rich compositional region (up to $\sim$38 mol% Zn) have the fcc disordered structure at high temperatures [10], known as α-brass. The atomic distribution, however, is not random. Different methods, e.g., neutron scattering [11], calorimetry [12], and first principles investigations [13] found that short-range order occurs in α-brass. A long range ordered Cu$_3$Zn-phase as found in other 3:1 alloys (e.g., Cu$_3$Au with L1$_2$-structure or Al$_3$Ti with DO$_{22}$-structure) was never detected experimentally. This is probably due to its low transition temperature. First principles studies proposed either an ordered DO$_{23}$-structure below 295 K [13] or an ordered L1$_2$-structure below 288 K [14].

The excess vibrational entropy may have large effects on phase stability calculations (for a review, see for example [15,16]). For describing the excess vibrational entropy, a bond length versus bond stiffness interpretation [15] was proposed. According to this interpretation, changes in the stiffness of a chemical bond are mainly produced by changes of the bond lengths, which occur with compositional variations. Such a relation was found for the Pd-V and Ni–Al systems using first principles methods [17,18]. A substitution of an atom of different size produces both bond softening of the smaller atom and bond stiffening of the larger atom. However, one of both effects may dominate the vibrational behaviour of the solid solution giving rise to excess vibrational entropies. Recently, a simple relationship was presented [19] for estimating the

TABLE 1

The maximum extent of the excess vibrational entropy ($\Delta_{max}S_m^{exc}$) as a function of the differences between end member volumes ($\Delta V_{i,m}$) and the differences between end member bulk moduli (ΔK_i) for three Mg–Ca substituted materials. The values for $\Delta_{max}S_m^{exc}$ and $\Delta V_{i,m}$ are normalised to a substitution of one atom.

	$\Delta V_{i,m}/$ $(10^{-5} m^3)$	$\Delta K_i/$ $(10^9 Pa)$	$\Delta_{max}S_m^{exc}/$ $(J \cdot mol^{-1} \cdot K^{-1})$
$(Mg,Ca)_3Al_2Si_3O_{12}$	0.40 [24]	−1 [24]	+1.0 [25]
$(Mg,Ca)O$	0.55 [26]	−50 [27,28]	~0[a]
$(Mg,Ca)CO_3$	0.88 [30]	−72 [30]	~0 [b]

[a] A first principles study [29] proposed low vibrational effects when comparing the results with experimentally determined phase stabilities.
[b] A theoretical study [31] found agreement with experimental data without including vibrational effects.

maximum extent of the excess vibrational entropy ($\Delta_{max}S_m^{exc}$). The functionality of this relationship can be described by comparing the stiffness of the end members and distinguishing two different cases. Case 1: The larger end member is elastically stiffer. In this case, the atoms of the smaller end member have to enlarge their bond lengths in the solid solution to a high degree. Their bonds are strongly softened, which generates positive excess vibrational entropies. Case 2: The smaller end member is much stiffer. These conditions produce strongly compressed bonds of the atoms of the larger end member and in consequence negative excess vibrational entropies. To calculate $\Delta_{max}S_m^{exc}$, the relationship uses the differences of the end member volumes ($\Delta V_{i,m}$) and the differences of the end member bulk moduli (ΔK_i), i.e.,

$$\Delta_{max}S_m^{exc}/(J \cdot mol^{-1} \cdot K^{-1}) = (\Delta V_{i,m}/(J \cdot mol^{-1} \cdot Pa^{-1}) + m\Delta K_i/Pa)f. \quad (1)$$

Based on data of silicate solid solutions and binary alloys, the parameters m and f of this equation were determined to be $m/(J \cdot mol^{-1} \cdot Pa^{-2}) = 1.089 \cdot 10^{-16}$ and $f/(Pa \quad K^{-1}) = 2.505 \cdot 10^5$ (after converting the values of [20] into SI units). $\Delta V_{i,m}$ is defined to be positive whereas ΔK_i has a positive or negative value separating the above described cases. If the larger end member is elastically softer, then ΔK_i values are defined to be negative and vice versa. The behaviour of the excess vibrational entropy can for example be demonstrated by comparing some Mg–Ca substituted materials. As can be seen from table 1, the increasing volume mismatch does not necessarily generate increasing excess vibrational entropies. The increasing volume mismatch from $(Mg,Ca)_3Al_2Si_3O_{12}$ to $(Mg,Ca)CO_3$ is compensated by increasing negative ΔK_i values. There are also solid solution systems, which are characterised by a low volume mismatch, but large negative ΔK_i values comparable to those of $(Mg,Ca)CO_3$. This is the case for some metallic systems e.g., the Cu–Zn binary. Here, we expect negative excess vibrational entropies. Up to date, equation (1) was successfully applied to various silicate solid solutions [19,21,22], some binary alloys [20] and the NaCl–KCl binary [23]. The third aim of this paper is to test this relationship on α-brass.

2. Experimental methods

2.1. Cu–Zn samples

The CuZn15 sample was kindly provided by Austria buntmetall, Amstetten, Austria. The CuZn34 sample is from Alu-point, Harsum, Germany. The samples were examined by scanning electron microscopy detecting no compositional inhomogeneities. The compositions of the samples are listed in table 2. The structure of the samples was investigated by X-ray diffraction in order to check for the presence of the bcc-alloy. No bcc-reflections were found.

TABLE 2

Electron microscope analyses in atomic%. The standard deviation is given in parentheses and refers to the last digit. The sample name represents weight%.

Sample	Cu	Zn
CuZn15	85.6 (2)	14.4 (2)
CuZn34	66.5 (2)	33.5 (2)

2.2. Relaxation calorimetry (PPMS)

Low-temperature heat capacities from 5 K to 300 K were measured using a commercially available relaxation calorimeter (heat capacity option of the PPMS by Quantum Design®). Pieces with ca. $4 \times 4 \times 0.3$ mm (~50 mg) were polished and mounted onto the calorimeter platform using Apiezon N grease. The measurements were repeated if the sample coupling, a measure of the quality of the thermal contact between sample and calorimeter platform, was lower than 90% (for details of the relaxation technique, see e.g., [32,33] and references therein). In such cases, the surface of the Cu–Zn pieces was reprocessed until a good sample coupling was achieved. It was found, however, that the PPMS measured heat capacities do not depend on the sample coupling, as it is the case when measuring oxide materials e.g., [34,35]. The accuracy of the PPMS heat capacities from $T = 100$ K to 300 K and the entropy at 298.15 K measured on single-crystal and sintered powder samples were found to be better than 0.5% [36].

2.3. Differential scanning calorimeter (DSC)

The heat capacity between $T = 300$ K and 573 K was measured using a power compensated Perkin Elmer Diamond DSC® on samples weighing ca. 150 mg. The DSC measurements were performed under a flow of Ar gas, with the calorimeter block kept at 250 K using a Perkin Elmer Intracooler. Each measurement consisted of a blank run with empty calorimeter chambers and a sample run, where the Cu–Zn sample and a pure Cu sample (with the same mass as the Cu–Zn sample and a purity of 99.8%) as reference material was placed into the calorimeter. The heat flow data (difference in heating power between the two chambers) were collected using a temperature scan (heating rate of 6 and 3 K/min) and isothermal periods of 3 min before and after the temperature scan. The heat flow versus temperature data from the sample run were shifted and rotated until the data of the isothermal periods agreed with those of the blank run (for details see e.g., [33]). The data from the blank run were then subtracted from those of the sample run to give the net heat flow of the sample. For calculating the heat capacity, the net heat flow data were finally divided by the heating rate and the mass of the sample. The accuracy of the DSC heat capacity data was determined to be better than 0.6% [33].

2.4. Evaluation of the raw heat capacity data

To calculate the vibrational entropy, the measured low temperature heat capacities were integrated numerically using an interpolation function of Mathematica® (interpolation order 2). The relative uncertainty of the entropy derived from the PPMS heat capacity data amounts to 0.2% for single-crystal and sintered powder samples as determined by a Monte Carlo technique in a previous study [37].

2.5. Calculations using density functional theory (DFT)

Quantum–mechanical calculations were based on the DFT plane wave pseudopotential approach implemented in the CASTEP code [38] included in the Materials Studio software from Accelrys®. The calculations were performed using the local density