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A relationship to estimate the excess entropy of mixing: Application in silicate solid solutions and binary alloys

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ABSTRACT

The paper presents new calorimetric data on the excess heat capacity and vibrational entropy of mixing of Pt–Rh and Ag–Pd alloys. The results of the latter alloy are compared to those obtained by calculations using the density functional theory. The extent of the excess vibrational entropy of mixing of these binaries and of some already investigated binary mixtures is related to the differences of the end-member volumes and the end-member bulk moduli. These quantities are used to roughly represent the changes of the bond length and stiffness in the substituted and substituent polyhedra due to compositional changes, which are assumed to be the important factors for the non-ideal vibrational behaviour in solid solutions.

1. Introduction

The standard entropy ($S^{298.15}$) of a perfect crystal can be derived from heat capacity (C_P) measurements ranging from 0 to 298.15 K because the entropy of a perfect crystal approaches zero when the temperature approaches zero K, i.e., the configurational part of the entropy (structural disorder) is zero. The temperature dependence of the entropy is given by the integral of $C_P/T\,dT$ and contains mainly the vibrational part of the entropy. Beside the vibrational entropy, the integral $C_P/T\,dT$ may also contain magnetic, electronic and other contributions (e.g., contributions from structural phase transitions). In solid solutions, the configurational entropy is unequal to zero and the heat capacity versus composition behaviour generally deviates from a linear relationship, especially at low temperatures of ~50 K. This deviation gives rise to excess heat capacities of mixing and in consequence to excess vibrational entropies of mixing. These excess quantities are significant in several binary alloys [1], but also in silicate solid solutions like alkali feldspars ($NaAlSi_3O_8$–$KAlSi_3O_8$), garnets ($Mg_3Al_2Si_3O_{12}$–$Ca_3Al_2Si_3O_{12}$), and in plagioclases ($NaAlSi_3O_8$–$CaAl_2Si_2O_8$) [2–4].

The physical nature of the excess vibrational entropy is still poorly understood. The excess entropy was correlated with the excess enthalpy of mixing in liquid binary alloys [e.g., 1, 5]. Such a relationship was also proposed by computer simulation studies performed on alkali halide, metallic and oxide systems [6,7]. Some light was shed on the physical nature of the excess vibrational entropy by Van de Walle and Ceder [8], who gave an overview of the suggested microscopic mechanisms. Substituting an atom by another atom of different size leads to strain fields. The smaller atoms get under tension, the larger one under compression. Beside this size mismatch effect, the bond stiffness was proposed to be an important factor [9,10]. To explain these relationships, Benisek and Dachs [10] distinguished three cases for a solid solution AC—BC:

- The B—C bonds are longer and elastically stiffer than the A—C bonds. Due to the elastically stiffer nature of the B—C bonds, their inter-atomic distances will not change as much as that of the A—C bonds with varying composition. Considering the changes from the end-member structures, the increase in A—C bond length is thus more pronounced than the decrease in B—C bond length. This behaviour is illustrated in Fig. 1. Atom A will find itself in a highly enlarged structure. Hence, the A—C bonds are softened in the solid solution and consequently, the mean frequencies of the vibrations are lowered. Vibrations with lower frequencies are excited at lower temperatures, and this behaviour generates positive excess heat capacities and vibrational entropies of mixing.
- In cases where the stiffness of the A—C and B—C bonds is similar but B—C bonds are again longer than A—C ones, the magnitude of A—C bond length increase is more pronounced than the decrease in B—C bond lengths (considering bond length changes

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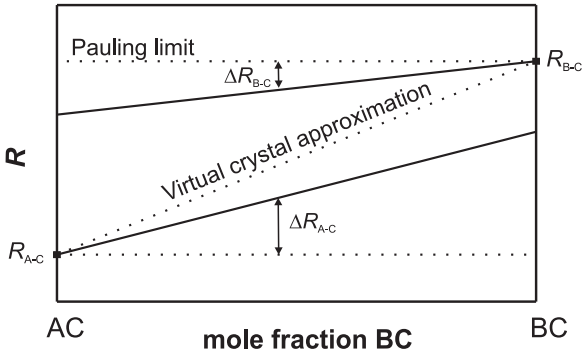

Fig. 1. Mean bond length (R) in a solid solution consisting of components AC and BC. *Heavy lines* show the changes of R with compositional changes. It represents cases, where the decrease of the larger polyhedron (ΔR_{B-C}) is less pronounced than the increase of the smaller one (ΔR_{A-C}). *Broken lines* represent the two limiting cases, Pauling limit and virtual crystal approximation.

from the end-member structures). This follows from the typical asymmetric dependence of the potential energy on the interatomic distance energetically favouring elongated bond lengths, when compared to compressed ones. Consequently, the softening of A—C bonds is again more pronounced than the stiffening of B—C bonds and positive excess heat capacities and vibrational entropies of mixing are produced.

- B—C bonds are longer but elastically softer than A—C bonds. The elastically stiffer A—C bonds force the B—C bonds to shorten to a higher extend compared to the other cases. The magnitude of bond softening may be similar to that of bond stiffening or even smaller. The effect on the entropy tends to be compensated or it results in even negative excess vibrational entropies.

Based on the cases discussed above, Benisek and Dachs [10] described the maximum values of the excess vibrational entropy ($\Delta_{max}S^{exc}$) by relating them to the difference in the end-member volumes (ΔV_i) and to the difference in the end-member bulk moduli (ΔK_i). ΔK_i was chosen to be negative, if the end-member with the larger volume had a lower bulk modulus and vice versa. Positive, zero or negative ΔK_i values thus represented the different cases mentioned above. Although ΔV_i and ΔK_i may not reflect the actual differences in length and stiffness of A—C and B—C bonds, they were sufficient to describe $\Delta_{max}S^{exc}$ of some silicate solid solutions.

The objective of this paper is to investigate, if this simple relationship can also be applied to binary alloys. For this purpose, two of such alloys (Ag–Pd and Pt–Rh) were investigated by relaxation and differential scanning calorimetry. To enlarge the data set, the excess entropy of mixing of binary alloys from Kubaschweski and Alcock [1] were used, where excess enthalpy, entropy and Gibbs free energy values are compiled for many binary alloys. Their entropy data were generally determined by the evaluation of calorimetric solution experiments (ΔH) and phase equilibrium experiments (ΔG).

2. Experimental methods

2.1. Relaxation calorimetry

Low temperature heat capacities were measured using a commercially available relaxation calorimeter (heat capacity option of the PPMS by Quantum Design®) from 5 to 300 K (for details of the technique, see e.g., [11] and references therein).

2.2. Differential scanning calorimetry (DSC)

High temperature heat capacities were measured using a Perkin Elmer Diamond DSC® from 280 to 800 K. The evaluation of the DSC raw data was performed as described in [12].

2.3. Binary alloys

An $Ag_{69.7}Pd_{30.3}$ sheet (~30 mg) and a $Pt_{55.2}Rh_{44.8}$ wire (~60 mg) were used for the calorimetric measurements. The Ag–Pd alloy was manufactured by Ögussa®, and the Pt–Rh alloy was obtained from Conatex®.

2.4. Calculations using the density functional theory (DFT)

The quantum-mechanical calculations presented here were based on the DFT plane wave pseudopotential approach using the CASTEP software [13] included in the Materials Studio software from Accelrys®. The calculations were performed using the local density approximation (LDA) [14]. Alternatively, the gradient-corrected functional (GGA-PBE) from Perdew et al. [15] was used. An ultrasoft and alternatively a norm-conserving pseudopotential were used to calculate the wave-functions of the ion core. Lattice dynamics calculations were based on the finite displacement approach, implemented in CASTEP, which calculates the forces on perturbed configurations in a supercell with positive and negative displacements. This enables the analysis of the asymmetry of the potential well and thus the study of anharmonic effects [16]. This can be done by increasing the atomic displacement from the default value of 0.0053 Å, which corresponds to the harmonic approximation, to higher values (personnel communication with S.J. Clark, University of Durham). The heat capacities of the end-members were calculated applying the same calculation parameters and structures (i.e., super cell with P1 symmetry) as used for the solid solutions. For each substance (Ag, Pd, $Ag_{75}Pd_{25}$), the calculations were performed several times increasing the precision of the calculation until the excess heat capacity values converged.

3. Results and discussion

3.1. Calorimetric results on Pt–Rh and Ag–Pd alloys

The raw C_P data of $Pt_{55.2}Rh_{44.8}$ and $Ag_{69.7}Pd_{30.3}$ have been deposited as electronic supplementary material linked to this article. The excess heat capacity of mixing is defined as

$$\Delta C_P^{exc} = C_P^{AB} - (C_P^A \cdot X_A + C_P^B \cdot X_B) \quad (1)$$

using mole fractions (X) of components A and B. The heat capacities for the low temperature region of the end-members were taken from the National Bureau of Standards [17,18] and those for the high temperature region were taken from Barin and Knacke [19]. These data allowed the calculation of ΔC_P^{exc} from the measured heat capacity of $Pt_{55.2}Rh_{44.8}$ and $Ag_{69.7}Pd_{30.3}$. The $Pt_{55.2}Rh_{44.8}$ alloy is characterised by small negative excess heat capacities (<0.2 J mol^{-1} K^{-1}) at low temperatures (<60 K) and by positive excess heat capacities (not exceeding 0.5 J mol^{-1} K^{-1}) at temperatures between 60 and 800 K. The resulting excess vibrational entropy is positive and amounts to ΔS^{exc} = 0.5 J mol^{-1} K^{-1} at 800 K. The entropy composition behaviour along this binary was assumed to be symmetric so that a maximum excess vibrational entropy, $\Delta_{max}S^{exc}$ = 0.5 J mol^{-1} K^{-1} is proposed for this binary.

The $Ag_{69.7}Pd_{30.3}$ alloy has negative excess heat capacities below 450 K, characterised by two negative peaks at ~50 and ~270 K, shown in Fig. 2. The calculated excess vibrational entropy at 450 K is ΔS^{exc} = −1.4 J mol^{-1} K^{-1}. Because the Ag–Pd alloy shows symmetric excess entropy behaviour [1], our calorimetrically determined value was used to calculate the maximum excess entropy for Ag–Pd alloys. Our calculations using the Margules mixing model yield $\Delta_{max}S^{exc}$ = −1.7 J mol^{-1} K^{-1}. This value is slightly less negative compared to the value given by Kubaschewski and Alcock [1] ($\Delta_{max}S^{exc}$ = −1.84 J mol^{-1} K^{-1}). Their data evaluation used the configurational entropy (S^{cfg}) of a fully disordered distribution. Possible short range ordering in the phase equilibrium experiments used in their evaluation might be responsible for the difference to our calorimetrically determined value. This is because short range ordering generates negative excess configurational entropies of mixing, i.e., the short range ordered phase has a somewhat lower S^{cfg} compared to the disordered structure. Ordering phenomena in Ag–Pd alloys were also reported by first principles studies [e.g., 20, 21].