ELSEVIER

Thermochimica Acta 311 (1998) 213–216

thermochimica acta

DSC and X-ray measurements as methods to detect lattice distortions

K. Sigrist*

Leipziger Str. 40, D-10117 Berlin, Germany

Received 20 May 1997; received in revised form 18 November 1997; accepted 3 December 1997

Abstract

The homogeneous lattice distortions in the crystals of several cubic, tetragonal and hexagonal metals, estimated from literature data, can be principally detected by DSC measurements and X-ray studies. Therefore, using these methods, it should be possible to effortlessly modify a theory of inhomogeneous and homogeneous lattice distortions, which has existed for ca. 10 years, by further planned experimental examinations. © 1998 Elsevier Science B.V.

Keywords: DSC; Lattice distortions; Metals; X-ray study

1. Introduction

As is generally known, elastic deformations of a solid disappear if external deforming forces are removed. But under certain conditions, a small quantity of deformations can remain in the solid after a deformation in the shape of inhomogeneous and homogeneous lattice distortions [1,2].

The inhomogeneous lattice distortions represent little chance deviations from the strict periodicity in the crystal lattice. They can be determined from the integral line widths of the X-ray interferences of the given material.

Homogeneous distortions exist if in a certain direction of the crystal lattice positive or negative deviations from the strict periodic structure are predominant. They can be determined by comparison of X-ray investigations of the deformed with those of the non-deformed material because of small differences of the diffraction angles.

For a homogeneous distortion, α can be defined as

$$\alpha = (a_\mathrm{d} - a_0)/a_0, \tag{1}$$

where a_d and a_0, respectively, are the lattice parameter of the deformed and the non-deformed material in direction of the crystallographic axis a.

The lattice distortions are linked with excess values of the thermodynamic functions, for example the internal energy, the entropy and the free energy. The phrase 'excess value' already shows that the relevant solid does not exist in the thermodynamic equilibrium. But it is in a metastable state, that means in a relatively stable state which corresponds to a minimum of the excess free energy [2].

Until now experimental studies of homogeneous distortions have only been carried out with MgO powders [1]. X-ray and solution enthalpy investigations have shown that, for example, a homogeneous distortion equal to -0.00017 results in an excess enthalpy of 434 J cm^{-3}. In contrast with this value, the maximum excess enthalpies of the inhomogeneous distortions and of the surface was found to be 107 and 544 J cm^{-3}, respectively.

---

*Corresponding author. Tel.: +49 30 2040491.

PII S0040-6031(97)00473-5

The results of the experimental investigations of MgO agree with the theoretical conception of the homogeneous and inhomogeneous distortions. But for an additional progress in this field further additional experimentation with other substances is needed.

Following the concept of homogeneous lattice distortions, the excess energy should also cause a change of melting enthalpy. The latter can be determined by DSC more easily than solution enthalpies. Thus, a comparison of X-ray diffraction and melting enthalpy measurements of samples of different pretreatment (to generate different amounts of lattice distortions) should eventually provide additional information concerning homogeneous lattice distortions.

As a first approach, this paper will present suggestions to choose suitable materials for the energetic and X-ray detection of homogeneous and inhomogeneous lattice distortions and estimations of the expected effects.

2. The selection of the substances and the estimate of the expected influences

Inhomogeneous distortions are unavoidably contained in all real crystals. For this reason, they will not be specially considered for the following selection of the appropriate substances in further experimental studies in the field of distortions. However, as was theoretically derived [2], homogeneous distortions can only exist in isotropic, cubic, tetragonal (Laue group TI) and hexagonal materials. Therefore, one criterion for the selection of the appropriate substances was their belonging to these crystal systems. On the other hand, one should prefer such substances having well-known melting characteristics, and easy to investigate by DSC, e.g. the reference materials for the calorimetric calibration of DSC instruments [4,5]. Among them, those listed in Table 1 also fulfil the first criterion, too.

Table 1
Temperature [a] and melting enthalpy [a] at the melting point for five metals used as DSC calibration standards

Metal	Temperature (K)	Enthalpy ($\mathrm{J\ cm^{-3}}$) [b]	Crystal system
In	425.7	209.2	Tetragonal [c]
Cd	594.2	477.9	Hexagonal
Pb	600.6	262.1	Cubic
Zn	692.6	775.4	Hexagonal
Al	933.5	1074.9	Cubic

[a] Refs. [3–5].
[b] This form corresponds to the energy density of elastic deformations [2].
[c] Laue group TI.

The starting point for estimating the expected caloric effects should be investigations of the zero point entropy of activated solids, which comes to a maximum of ca. 30% of the melting entropy [6]. Correspondingly, we can assume that the maximum excess internal energy of such solids caused by structure disruptions and an extended specific surface also amounts to ca. 30% in relation to the enthalpy of melting.

The total excess energy obtained experimentally by the already mentioned investigations with MgO [1,2] resulted in a maximum of ca. 16% in relation to the melting enthalpy of MgO (6815 $\mathrm{J\ cm^{-3}}$ [7]), roughly half the theoretically estimated upper value of 30%. Therefore, it seems that the energy part for the homogeneous distortions could increase beyond that in the given example by other preparation conditions. Because the MgO samples were powders, i.e. mixtures of different single crystals, it can be assumed that these already contained both crystals with less but also crystals with more distortions.

For a minimum of the excess free energy of homogeneous distortions certain conditions are valid. In the tetragonal and hexagonal materials result [2]

$$\beta = -\alpha \tag{2}$$

and in cubic substances

$$\gamma = -(\alpha + \beta) \tag{3}$$

if α, β and γ mean the homogeneous distortions in the direction of the principal axes a, b and c of the elementary cell.

An estimate of the expected lattice distortions α and β is based on the following equations (for the definition of h, k, l, a, c and d, see Ref. [8] or other textbooks of crystallography):

for cubic materials

$$(h^2 + k^2 + l^2)a^{-2} + 2(l^2 - h^2)\alpha a^{-2} + 2(l^2 - k^2)\beta a^{-2} = d^{-2} \tag{4}$$

for tetragonal materials

$$(h^2+k^2)a^{-2}+2(k^2-h^2)\alpha a^{-2}+l^2c^{-2}=d^{-2} \tag{5}$$

for hexagonal materials

$$4(h^2+k^2+hk)a^{-2}+8(k^2-h^2)\alpha a^{-2} + 3l^2c^{-2}=3d^{-2} \tag{6}$$

These equations result from the Bragg quadratic equations [8], using Eqs. (2) and (3), respectively, and are followed by a Taylor series expansion with respect to α and β up to linear terms at $\alpha=\beta=0$ because the α and β are assumed small. Using the appropriate equation, both the lattice parameters (a and c) and the homogeneous distortions (α and β) can be obtained by regression analysis of suitable determinations of the d values.

By checking data in the available literature, an effort to find hints for homogeneous lattice distortions inherent in the metals of Table 1 was made. For this purpose, X-ray investigations for the determination of lattice parameters of metal powders were used [9,10].

As only one sample of each metal in Table 1 was tested, this method of checking has an accidental character. But by chance, the test for one of the five powders was successful, namely the proved Zn sample (cf. [9], p. 16) showed a detection result reliable for homogeneous distortions (statistical probability $P=0.95$).

For the regression analysis of the d values, two variants are possible:

(i) with the assumption that there are homogeneous distortions in the powder ($\alpha\neq0$) using Eq. (6)
(ii) with the assumption that there are no homogeneous distortions in the powder ($\alpha=0$) using Eq. (6) without the second term.

3. Results

(i) $a=(0.2664345\pm0.0000053)$ nm;
$c=(0.4947133\pm0.0000067)$ nm;
$\alpha=(0.000100\pm0.000030)$
(ii) a=(0.2664494 ± 0.0000028) nm;
$c=(0.4947160\pm0.0000069)$ nm

It must be emphasized that with the given precision of the values resulting from the regression analysis (confidence interval at $P=0.95$), only the relative position of the X-ray interferences are characterized. The absolute values depend, moreover, on the precision of other indirectly used quantities, e.g. the wavelength of the X-ray radiation.

It follows for variant (i) that the α value is three times as big as its confidence interval and that it is of the same order of magnitude as the homogeneous distortion found for MgO. If a comparison of both the variants (i) and (ii) is made, the result regarding the lattice parameter '*a*' is that there is a reliable difference but regarding '*c*' there is no such difference.

4. Conclusions

As shown by means of the X-ray data, homogeneous lattice distortions can exist in metals in the same order of magnitude as in MgO. This also should be valid for the corresponding excess values of the internal energy, which came for MgO to ca. 6% of the heat necessary for melting. Differences of this order of magnitude in relation to the main effect can be measured without too much effort with modern DSC equipment [5].

Stronger effect could be anticipated, e.g. from the choice of suitable crystals from a larger number of single crystals. For this purpose a lot of these crystals must be prepared. But, for the DSC as also for the structure measurements, they can be fairly small [8].

Therefore, it should be possible not only to determine the conditions for the growth of the crystals as the optimum cooling rate and undercooling but also to grow them directly in a DSC crucible and instrument by preceded experiments. From those crystals which exhibit the strongest X-ray effects, the melting heat should then be determined by DSC. This way the correlation between the structure defects and the excess energy could be investigated.

The melting of metals is frequently used for the heat calibration of DSC instruments. In contrast to the requirements for the study of distortions as proposed here, one needs materials free of distortions, if possible, for calibration measurements. However, important hints concerning lattice distortions can be expected from careful evaluation of calibration experiments, especially from comparisons of first and subsequent runs of the same sample.

Acknowledgements

The author would like to thank Dr. D. Schultze (Bundesanstalt für Materialforschung und prüfung, Berlin) and Prof. Dr. U. Steinike (Institut für Angewandte Chemie, Berlin) for their helpful discussions of the problems and for valuable hints regarding the choice of the suitable substances.

References

[1] K. Sigrist, H. Fichtner, Phys. Stat. Sol (a) 95 (1983) 473–481.
[2] K. Sigrist, Z. Phys. Chem. (Leipzig) 271 (1990) 297–308.
[3] S.M. Sarge, E. Gmelin, G.W.H. Höhne, H.K. Cammenga, W. Hemminger, W. Eysel, Thermochim. Acta 247 (1994) 129–168.
[4] W.F. Hemminger, H.K. Cammenga, Methoden der Thermischen Analyse, Springer-Verlag, Berlin, 1989, p. 181.
[5] W.W. Wendlandt, Thermal Analysis, John Wiley & Sons, New York, 1986, p. 276, 281, 394.
[6] K. Torkar, Proceedings of the 4th International Symposium Reactivity of Solids, Amsterdam, 1961, p. 400–408.
[7] W. Auer, H. Kienitz, in: Landolt-Börnstein: Zahlenwerte und Funktionen in Natur und Technik, 6. Auflage, Bd. II/4, Springer-Verlag, Berlin/Göttingen/Heidelberg, 1961, p. 209.
[8] W. Massa, Kristallstrukturbestimmung, Teubner-Verlag, Stuttgart, 1994, p. 35, 88.
[9] Swanson and Tatge, Natl. Bur. Stand. (U.S.), Circ. 539, I (1953) 11, 16, 34.
[10] Swanson and Fuyat, Natl. Bur. Stand. (U.S.), Circ. 539, III (1954) 10, 12.