Journal of Thermal Analysis, Vol. 33 (1988) 279–284

THE USE OF CALORIMETRIC DATA FOR ESTIMATION OF THE POINT DEFECT CONCENTRATION IN SOLIDS

N. F. Uvarov and *E. F. Hairetdinov*

INSTITUTE OF SOLID-STATE CHEMISTRY, SIBERIAN BRANCH OF THE USSR ACADEMY OF SCIENCES, NOVOSIBIRSK 91, DERZHAVINA 18, U.S.S.R.

Calorimetric methods which allow estimation of the point defect concentration in solids are reviewed. Special attention is paid to the calculation of defect parameters based on the analysis of excessive heat capacity, and to correlations between the thermodynamic parameters of melting and the energetic parameters of point defect formation. The applicability of the thermodynamic approach to the study of intrinsic disorder in solids is demonstrated.

A variety of physical properties may be estimated by using calorimetric data. Among them, the specific heat capacity and the enthalpies and temperatures of phase transitions may be of use for the estimation of parameters of point defects in solids.

The temperature-dependence of the concentration of point defects in a crystal may be presented as:

$$n(T) = N \exp(S_o/zk) \exp(-H_o/zkT) \tag{1}$$

where S_o and H_o are the entropy and enthalpy of the defect formation process, z is the number of species in the defect, N is the Avogadro number and k is Boltzmann's constant. For Schottky defects, $z = 1$ or $z = 2$ for simple and binary substances respectively and for Frenkel defects $z = 2$. From Eq. (1), the following expression holds for the excess heat capacity associated with defect formation:

$$c_p^{\mathrm{d}} = \frac{\mathrm{d}}{\mathrm{d}T}(H_o\, n(T)) = (A/T^2) \exp(-H_o/zkT) \tag{2}$$

where $A = (N H_o/zk) \exp(S_o/zk)$. In contrast with the Debye law ($c_p^o \to 3R, T > \theta_D$) and the contribution due to anharmonicity ($c_p^a \cong \alpha T$), c_p^{d} in Eq. (2) increases exponentially with temperature. At premelting temperatures $T \cong T_m$, the c_p^{d} contribution to c_p may be high enough to be detectable. A computer-assisted fit of the experimental data to the theoretical expression:

$$c_p = \theta(T) + \alpha(T) + (\beta/T^2) \exp(-\delta/T) \tag{3}$$

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

where $\theta(T) = c_p^o$ and $\alpha(T) \doteq c_p^a$, makes it possible to estimate the values of $n(T)$, H_o and S_o. It has been demonstrated [1] that c_p^d in AgCl and AgBr are high, and concentrations of point defects estimated in accord with Eq. (3) are in fair agreement with those obtained from conductivity data. In a similar way, the point defect concentration may be evaluated for molecular solids as well as for metals.

In superionic solids with fluorite structure (CaF_2, $SrCl_2$, PbF_2, etc.), all the phase transition enthalpy is shown to originate from the generation of Frenkel defects in the anion sublattice [2]. Values of H_o estimated from the slope of the $\ln(c_p T^2)$ *vs.* $1/T$ plot are in excellent agreement with those obtained from conductivity measurements [3, 4].

Quite a different approach to the estimation of crystalline disorder is based on the analysis of entropies S_m and enthalpies H_m of melting. The relations are known between H_o and crystal lattice energy [3], between H_o and T_m [6, 7], etc. As shown earlier [8, 9] a more precise and universal correlation holds between H_o and H_m:

$$H_o = (8.6 \pm 0.6) H_m \tag{4}$$

which is demonstrated in Fig. 1. This correlation may be treated in terms of the model of quasicrystalline liquid containing a fraction x_L of defects with relaxed surroundings around them [8–11].

Let the crystal energy U_1 of a simple solid have the form

$$U_1 = 1/2 \sum_i \gamma(r_i) \; \varphi(r_i) \tag{5}$$

where $\gamma(r_i)$ is the coordination number of the i-th sphere around a chosen atom, and $\varphi(r_i)$ is the interatomic potential. As a first approximation, we shall ignore the possible temperature-dependence of $\varphi(r_i)$. The energy of quasicrystalline melt in this approximation may be presented as

$$U_2 = 1/2 \sum_i \gamma(r_i) \, \varphi(r_i) \; (1-x_L) + W(1-x_L) \tag{6}$$

Here, the term $W(1-x_L)$ corresponds to the relaxation of the quasicrystalline lattice around the defects, i.e. to small displacements of atoms, resulting in the disappearance of the long-range order in a melt. One can write W in the form

$$W = 1/2 \sum_i \left[\frac{d\varphi(r_i)}{dr} \Delta r_i + \frac{1}{d} \frac{d^2 \; \varphi(r_i)}{dr} \Delta r_i^2 \right] \gamma(r_i) \tag{7}$$

where Δr_i is the displacement distance for the atom. Let the temperature-dependence of U_2 (and of U_1) be ignored. The Gibbs free energies for the crystal and the melt may be presented as $G_1 = U_1 - 3RT\ln(hw_1/kT) + pV_1$, and $G_2 = (U_1 + W)(1-x_L) - TS_c - 3RT\ln(hw_2/kT) + pV_2$, respectively. Here, w_1 and w_2 are the Debye frequencies for the crystal and the melt, V_1 and V_2 are the corresponding molar volumes, and S_c is the configurational entropy of the melt.

When $T = T_m$, then $G_1 = G_2$ leads to

$$H_m = U_2 - U_1 + p(V_2 - V_1) \tag{8}$$

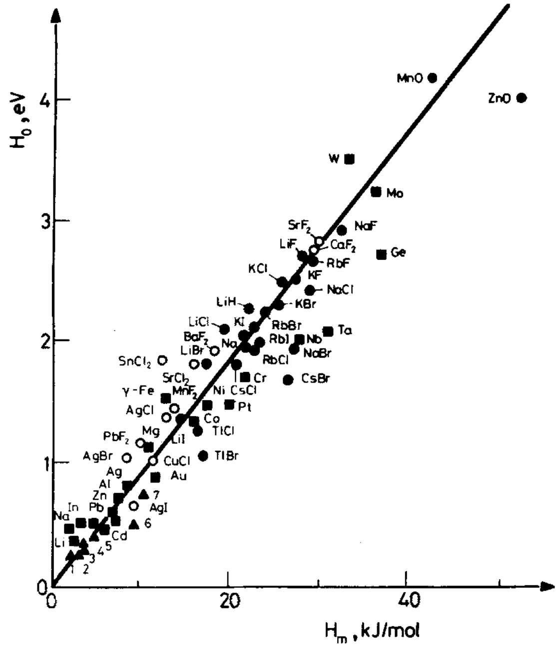

Fig. 1 Correlation between the defect formation enthalpy H_o and the enthalpy of melting for a series of ionic substances with Schottky (●) and Frenkel (○) disorder, for metals (■) and molecular organic compounds (▲). Solid line corresponds to Eq. [4].

1 – benzene;
2 – cis-1,2-dimethylcyclopentane;
3 – cyclooctane;
4 – 1,1-dimethylcyclohexane;
5 – 2,2,3-trimethylbutane;
6 – succinonitrile;
7 – adamantane;

For ambient conditions, the term $p(V_2 - V_1)$ is small and from Eq (5)–(6) the following expression is obtained:

$$H_m = U_1 x_L + W(1 - x_L) \tag{9}$$

On the other hand, the conventional theoretical calculations of H_o in solids start from the relation [12–14]

$$H_o = U_1 + W' \tag{10}$$

where W' is the polarization energy for the crystal lattice around a defect. Its value may be estimated by using an expression similar to Eq. (7). Assuming that nearest neighbour disorder around a defect in a crystal is energetically similar to that in the melt, one can write

$$W' = X(1 - x_L)/x_L \tag{11}$$

and from Eqs (10)–(11) the final expression for H_m follows:

$$H_m = x_L H_o \tag{12}$$

wich is equivalent to Eq. (4). Equation (12) compared with Eq. (4), states that $x_L = (11.6 \pm 0.8)$ mol% is nearly constant at $T = T_m$ for ionic, molecular and metallic melts and does not depend on the particular form of the interatomic potential.

For the entropy of melting one can obtain the following expression $S_m = \Sigma_i (S_c + 3R \ln (\nu_{1i}/\nu_{2i}))$, where summation must be done for all the sublattices, ν being the corresponding Einstein frequencies and subscripts 1 and 2 referring to the solid and molten states, respectively. In terms of this model, $S_c = (0.36 \pm 0.02)\ R$ for each sublattice. The change in vibration entropy for alkali halide type crystals may be expressed as $S_\nu = 3R \ln(\frac{\nu_{1c}\nu_{1a}}{\nu_{2c}\nu_{2a}})$, where ν_c and ν_a are the Einstein frequencies for the cation and the anion. We assume that the frequencies of atoms surrounding a defect in a solid are equal to the Einstein frequencies in melt. If so, the entropy of defect formation may be written as $S_o = \nu\, k \ln(\frac{\nu_{1c}\nu_{1a}}{\nu_{2c}\nu_{2a}})$, where ν is the number of ions around the defect with frequencies ν_{2c} and ν_{2a}. The vibrational contribution to the entropy of melting may therefore be written as $S_v = 3NS_o/\nu$. For a NaCl crystal, $S_m \simeq 3R$ and $S_o \simeq 10k$ result in $\nu = 3NS_o/S_v \simeq 13$, i.e. the disordered or "vibrationally melted" region is not more than two coordination spheres in size. Assuming $S_v \gg S_c$ a simple relation may be obtained, $S_m = 3NS_o/\nu$ [15], which leads to an expression for the defect concentration at the melting temperature n_m in the solid:

$$-\ln(n_m/N) = S_m/zR\,(1/x_L - \nu/3)$$

In conclusion, two possible applications of calorimetric data for estimation of the defect concentration in solids should be noted: analysis of the temperature-dependence of c_p in the vicinity of the melting or phase transition points, and analysis of H_m or S_m values. These calorimetric approaches are equally useful for the evaluation of defect-related properties of solids.

References

1 A. R. Ubbelohde, The Molten State of Matter, John Wiley & Sons, London, 1978.
2 M. O'Keeffe and B. G. Hyde, Phil. Mag., A33 (1976) 219.
3 W. Schröter, and J. Nölting, J. Phys. (Paris), 41 (1980) C6–20.
4 J. Oberschmidt, Phys. Rev., B23, (1981) 5038.
5 T. Gorecki, Z. Metallk. 65 (1974) 427.
6 L. W. Barr and A. B. Lidiard in Physical Chemistry, vol. 10, ed. by H. Eyring, D. Henderson and W. Jost, A. P., N., Y., 1970, p. 152.
7 J. Van-Liempt, Z. Phys., 96 (1935) 534.
8 N. F. Uvarov, E. F. Hairetdinov and V. V. Boldyrev, J. Solid State Chem., 51 (1984) 59.
9 N. F. Uvarov, E. F. Hairetdinov, Izv. SO AN SSSR, Ser. Khim., Nauk, n 8, vyp. 12, 1984, p. 4 (In Russian).
10 Y. I. Frenkel, Kinetic theory of liquids, Izd. AN SSSR, M., 1945 (In Russian).
11 I. D. Protasov, Zh. Fiz. Khim., 53 (1984) 554 (In Russian).
12 N. F. Mott and M. J. Littleton, Trans. Faraday Soc., 34 (1938) 485.
13 G. G. Fumi and M. P. Tosi, Disc. Faraday Soc., 32 (1952) 95.
14 C. R. A. Catlow, J. Corish, K. M. Diller, P. W. M. Jackobs and J. Norgett, J. Phys., C12 (1979) 451.
15 N. F. Uvarov, E. F. Hairetdinov, Izv. SO AN SSSR, Ser. Khim. Nauk, N 2, vyp. 4, 1986, p. 27 (in Russian).

Zusammenfassung – Kalorimetrische Methoden zur Abschätzung der Konzentration von Punktdefekten in Festkörpern werden zusammengestellt. Aufmerksamkeit verdienen die Berechnung von Defektparametern aus einer Untersuchung der Exzeß-Wärmekapazität und Korrelationen zwischen thermodynamischen Parametern des Schmelzens und energetischen Parametern der Punktdefektbildung. Die Anwendbarkeit eines thermodynamischen Ansatzes zur Untersuchung der Eigenfehlordnung in Festkörpern wird demonstriert.

РЕЗЮМЕ — Представлено обозрение калориметрических методов определения концентрации точечных дефектов в твердых телах. Особое внимание обращено на вычисление параметров дефектов, исходя из анализа избыточной теплоемкости и корреляций между термодинамическими параметрами плавления и энергетическими параметрами образования точечных дефектов. Показана применимость термодинамического подхода к изучению собственного беспорядка в твердых телах.