Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 431 (2005) 21–23
thermochimica acta
www.elsevier.com/locate/tca

Configurational entropy and possible plateau smaller than $R \ln 2$ in complex crystals

Kazuya Saito*, Yasuhisa Yamamura

Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan

Received 22 October 2004; received in revised form 19 November 2004; accepted 2 January 2005
Available online 13 February 2005

Abstract

Configurational entropy due to structural disorder in complex crystals is considered in some details. It is reminded that motional correlation and equivalence of plural entities (such as molecule or group) have potentially serious effects on the entropy. Possible appearance of entropy plateaus in its temperature dependence is suggested.

Keywords: Configurational entropy; Order–disorder transition; Supramolecular system

1. Introduction

Recently, complex molecular systems such as those with supramolecular architecture or self-assembled complexes attract increasing interests from their potential to provide multifunctional materials [1]. For successful application of thermodynamic approach to such systems new ways to extract useful information from experimental entropy S is highly desired to be found, though the Boltzmann principle, $S = k_B \ln W$ (k_B, Boltzmann's constant and W the number of microscopic states) surely holds for any systems. In this context, one of the present authors [2–5] recently proposed a new method of analysis, called the $\Delta_{trs}S$ analysis for compounds with long alkyl chains, which are often used as spacers between functional groups in supramolecular or assembling approach. As evident from the fact that the method is only applicable to compounds having long alkyl chain(s), the method is based on the molecular details of systems. One of the authors [6] also pointed out recently a relation between the change in vibrational entropy and thermal parameters observed by diffraction crystallography though the relation is within the harmonic approximation. In this paper, another direction is sought. The property we focus our attention upon in this paper is the relation between entities (molecule, group, etc.) comprising complex systems. The first is the motional correlation between plural entities and the second is the symmetry. In the following, the minimal possibility of disorder is assumed for the sake of clarity: the entity may have one additional configuration to that corresponding to the (non-degenerate) ordered state, which is energetically the ground level. According to the Boltzmann principle, therefore, the maximum (limiting) entropy is always $R \ln 2$ for an ensemble of particles of 1 mol. In actual applications, other contribution to entropy than structural disorder, such as lattice vibration, magnetism and degenerated Fermi liquid (conduction electrons/holes), should be subtracted from the experimental entropy.

2. Motional correlation

It is evident that the configurational entropy is reduced accordingly when plural entities are rigidly bound or their structural disorders are completely correlated. For example, if the disorder of n entities is completely correlated, the resultant entropy becomes $(R \ln 2)/n$. A classical example of this type is the problem of the residual entropy of ice [7–9], where the so-called "ice-rule" exerts a strong restriction on

---

* Corresponding author. Tel.: +81 298534239; fax: +81 298536503.
E-mail address: kazuya@chem.tsukuba.ac.jp (K. Saito).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.01.015

positional disorder of protons in hydrogen bonds between neighboring H_2O molecules. Although the correlation was detected through the residual entropy in this case of the *simple* molecule, it is generally difficult to do similarly on complex systems due to the difficulty in estimating spectroscopic entropy. On the other hand, such reductions in the configurational entropy can be found in the entropy of order–disorder transition of some compounds. The complex oxides, ZrW_2O_8 and HfW_2O_8, which show a negative thermal expansion in a wide temperature range [10,11], undergo an order–disorder phase transition concerning the orientation of WO_4 tetrahedra above room temperature. Although the conventional structure analysis [10,11] suggests two tetrahedra are involved per chemical formula in this order–disorder transition, the precise calorimetry detected $R\ln 2$, only a half of the expected entropy of transition. This can be rationalized if the two tetrahedra reorient themselves concertedly in a perfect fashion [12–14]. In a mixed-valence binuclear one-dimensional MMX chain compound, $Pt_2(MeCS_2)_4I$ [or written as $Pt_2(dta)_4I$], which is the first MMX showing metallic temperature dependence of conductivity [15], an order–disorder transition concerning the twist of the CS_2 moieties bridging two Pt atoms occurs at 373 K. Since the experimental entropy of transition is only $R\ln 2$, it was concluded that *four* CS_2 moieties are twisted concertedly [16]. In other words, the deviation from $R\ln 2$ in entropy reflects the motional correlation between plural entities. Although spectroscopic methods sense the particle dynamics in a very detailed manner, the information obtained is usually based on the single-particle scheme. In this respect, the thermodynamic approach utilizing the analysis of entropy has a possibility to put the research area beyond the single-particle description.

3. Effect of symmetry

If plural entities are located closely in space and are related by symmetry, a possible step (or plateau) may exist in temperature dependence of the configurational entropy. Suppose n entities are equivalent in the sense of the first sentence of this paragraph. The ordered state is assumed to be defined uniquely. A possible disorder located at the next higher energy is that in which one of n entities is misoriented. As the position of the misoriented entity is chosen from the n equivalent sites, the disordered states degenerate n times. At a temperature that is sufficiently high relative to the energy difference and low against higher energy levels (disorder), the entropy reaches the limiting magnitude, $[R\ln(n+1)]/n$. The n-dependence of this entropy step can be seen in Fig. 1.

To extend discussion in line to the higher levels of disorder, it is necessary to make some assumption to the energy of the upper levels. It is assumed here for simplicity that the energy of the disordered state is solely determined by the number of the misoriented entities. All the states are separated into $(n+1)$ energy states and n entropy plateaus can be imagined accordingly. The degeneracy of the disordered state with l misoriented entities is given by a simple combination ${}_nC_l$. A possible plateau corresponding to the saturated population below this states is given by

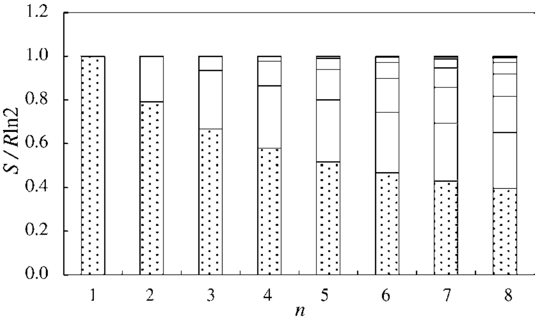

Fig. 1. Possible entropy steps in cases of $n = 1$–8. The height of the first step ($l = 1$) is shadowed for clarity.

$$S_l = \frac{R}{n}\ln\left(\sum_{i=0}^{l} nC_i\right)$$

Evidently, S_n fulfills the identity $S_n = R\ln 2$. In the case where the fully misoriented state is energetically equivalent to the fully ordered (ground) state, only plateaus below S_l ($l < n/2$) are of physical relevance.

Possible entropy steps are shown for $n = 1$–8 in Fig. 1. It is interesting that the first step is larger or comparable to a half of the full limit $R\ln 2$ in realistic cases with small or moderate n. Indeed, the first step becomes smaller than the half at $n = 6$.

Whether the steps are really observable or not depends on the energy separations. An rather unrealistic example is shown in Fig. 2, where the energy of the $(l+1)$th level with l misoriented entities are artificially given by $E_{l+1} = 5^{l-1}\Delta$ $(1 \le l \le 4)$with $E_1 = 0$ and $n = 4$. While symptoms of steps can be seen in Fig. 2, no clear step or plateau appears in this example having the exponential spacing of levels. Even so, we believe the present consideration contributes to deepen our understanding on complex systems. For example, if the experimental entropy of transition is smaller than the expected one upon a first-order order–disorder transition, the difference between the experimental and idealized entropies can be attributed to the disorder already excited below the transition temperature. If the difference is larger than one of

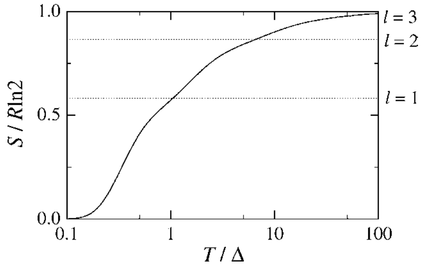

Fig. 2. Temperature dependence of entropy of a system with $n = 4$ where the energy of the $(l+1)$-th level with l misoriented entities are given by $E_{l+1} = 5^{l-1}\Delta$ $(1 \le l \le 4)$ with $E_1 = 0$.

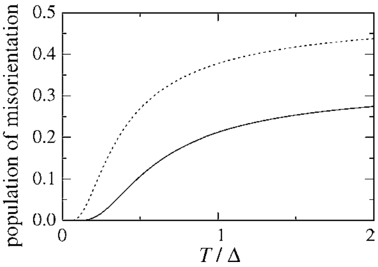

Fig. 3. Population of misoriented entities for two systems with seeming energy difference 0.5Δ for 1 mol of entities. Solid line: the degeneracy 1:2 and the energy difference Δ for 2 mol of entities ($n = 2$); dotted line: the degeneracy 1:1 and the energy difference 0.5Δ for 1 mol of entity ($n = 1$).

expected steps, it may be concluded that the disorder below the transition is stronger than that giving the corresponding plateau.

The following point should be noted. The energy is given for n entities in the above consideration. Although it may seem equivalent to, e.g., $10\,\mathrm{kJ\,mol^{-1}}$, it should be written as $20\,\mathrm{kJ}$ (2 mol of entity)$^{-1}$ if $n = 2$. Unless so, it will be understood as that for a single entity. Fig. 3 indicates this difference using a simple two level systems: solid line is the population at the upper level with the degeneracy 1:2 and the energy difference Δ (in the case of $n = 2$), while dotted line is that with the degeneracy 1:1 and the energy difference 0.5Δ (in the case of $n = 1$). The difference is evident between two cases. Conversely, this difference gives the possibility to distinguish them. Since the population of the misoriented entity can be determined by the conventional diffraction crystallography, it can be deduced which is adequate to describe the system under consideration from the temperature dependence of the population of the misoriented entity and the entropy. For example, consistent analysis of the step in heat capacity at a glass transition in relation to the experimental disorder obtained by the diffraction structure analysis means that the single-particle description assumed in the analysis was adequate for organic metals $(\mathrm{DMET})_2\mathrm{X}$ ($\mathrm{X} = \mathrm{BF_4}$ and $\mathrm{ClO_4}$) [17]. It is noted that there exists a special situation in the case of Fig. 3. Since the limiting population for $n = 2$ is 1/3, the system is classified to the case of $n = 1$, where the limiting population is 1/2, if the experimentally obtained population of the misoriented entity is beyond 1/3.

One may incline that the consideration here is realistic. A real case with large n such as 8 can be found: the room temperature phase of MMX complexes, $\mathrm{Pt_2(RCS_2)_4I}$ (R = propyl or butyl group), has a periodicity three in terms of a unit complex MMX in tetragonal system [18,19]. Two units of complex are crystallographically equivalent, resulting in the case with $n = 8$ assuming ligands are entities. Cases with n is a prime integer such as 5 or 7 in Fig. 1 will be rare because these numbers of equivalent entities are incompatible with standard lattice symmetries (three-dimensional space group). They may, however, be realized in quasicrystals.

4. Conclusion

Configurational entropy due to structural disorder in complex crystals is considered in some details. It was shown that motional correlation and equivalence of plural entities (such as molecule or group) have potentially some serious effects on the entropy. Possible appearance of entropy plateaus in its temperature dependence was suggested. Even if the plateaus are not seen in real systems, the present analysis provides a physical image of and a way to describe in words (not in mathematical formula) the partial disorder. Especially, the entropy smaller than the first plateau can be surely explained as follows: one or less entity in a group consisting of n entities is misoriented. This statement is evidently clear than the usual phrase that the average number of states is $\exp(S/R)$.

References

[1] J.-M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, Weinheim, 1995.
[2] A. Sato, Y. Yamamura, K. Saito, M. Sorai, Liq. Cryst. 26 (1999) 1185.
[3] K. Saito, T. Shinhara, T. Nakamoto, S. Kutsumizu, S. Yano, M. Sorai, Phys. Rev. E 65 (2002) 031719.
[4] K. Saito, M. Ikeda, M. Sorai, J. Therm. Anal. Calor. 70 (2002) 345.
[5] M. Sorai, K. Saito, Chem. Rec. 3 (2003) 29.
[6] K. Saito, S. Ikeuchi, A. Ota, H. Yamochi, G. Saito, Chem. Phys. Lett. 401 (2005) 76.
[7] W.F. Giauque, M. Ashley, Phys. Rev. 43 (1933) 81.
[8] L. Pauling, J. Am. Chem. Soc. 57 (1935) 2680.
[9] J.F. Nagle, J. Math. Phys. 7 (1966) 1484.
[10] T.A. Mary, J.S.O. Evans, T. Vogt, A.W. Sleight, Science 272 (1996) 90.
[11] J.S.O. Evans, T.A. Mary, T. Vogt, M.A. Subramanian, A.W. Sleight, Chem. Mater. 8 (1996) 2809.
[12] Y. Yamamura, N. Nakajima, T. Tsuji, Solid State Commun. 114 (2000) 453.
[13] Y. Yamamura, N. Nakajima, T. Tsuji, Phys. Rev. B 64 (2001) 184109.
[14] Y. Yamamura, T. Tsuji, K. Saito, M. Sorai, J. Chem. Thermodyn. 36 (2004) 525.
[15] H. Kitagawa, N. Onodera, T. Mitani, K. Toriumi, M. Yamashita, Synth. Met. 86 (1997) 1931.
[16] Y. Miyazaki, Q. Wang, A. Sato, K. Saito, M. Yamamoto, H. Kitagawa, T. Mitani, M. Sorai, J. Phys. Chem. B 106 (2002) 197.
[17] H. Akutsu, K. Saito, Y. Yamamura, K. Kikuchi, H. Nishikawa, I. Ikemoto, M. Sorai, J. Phys. Soc. Jpn. 68 (1999) 1968.
[18] M. Mitsumi, S. Umebayashi, Y. Ozawa, K. Toriumi, H. Kitagawa, T. Mitani, Chem. Lett. (2002) 258.
[19] M. Mitsumi, K. Kitamura, A.I. Morinaga, Y. Ozawa, M. Kobayashi, K. Toriumi, Y. Iso, H. Kitagawa, T. Mitani, Angew. Chem. 41 (2002) 2767.