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Interfacial Energies in Crystal Structure Transformations*

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Turnbull's theory of heterogeneous nucleation has been extended to obtain approximate values of interfacial energies γ in solids which exhibit reversible phase transformations. DTA curves of reversible transformations can be analysed in terms of the nucleation theory and with some reasonable assumptions, an estimate of γ can be obtained. A knowledge of the crystal structures of the two phases, along with the enthalpy of the transformation also affords a method of estimating γ-values theoretically. These three approaches have been applied to quartz, K_2SO_4, CsCl, NH_4Cl, and NH_4Br; the results have been compared.

1. Introduction

The interfacial energies between the transforming phases in liquid-solid transformations have been estimated for many materials by Turnbull [1, 2] on the basis of heterogeneous nucleation theory. Turnbull's nucleation theory has been extended by Natarajan, Das and Rao [3] to interpret the thermal hysteresis [4] and particle size effects in reversible crystal structure transformations. In the present study we have estimated the interfacial energies γ, in the solid-solid transformation by applying the nucleation theory to the transformation data obtained from DTA [4]. The transformations studied are: (i) $\alpha \rightleftharpoons \beta$ inversion of quartz; (ii) $\beta \rightleftharpoons \alpha$ transformation of K_2SO_4; (iii) Pm3m $\rightleftharpoons$ Fm3m transformations of CsCl, NH_4Cl, and NH_4Br; (iv) hexagonal $\rightleftharpoons$ cubic transformation of AgI. These values of γ have been compared with theoretical estimates obtained by extending a method illustrated by Bruce [5] for evaluating the interfacial energies in liquid-solid interfaces.

2. γ from Particle Size Variation

In Turnbull's [1, 2] theory of nucleation the nucleation rate can be represented as

$$R \simeq R_0 \exp\left(- A f(\theta)\, \gamma^3/\Delta T^2\right) \qquad (1)$$

where γ is the interfacial energy; ΔT equals $|T_0 - T|$ and

$$A = \frac{16\pi T_0^2}{3kT\Delta H_V^2};$$

T_0 is the equilibrium transformation temperature; ΔH_V is volumetric heat of transformation and $0 < f(\theta) < 1$.

For observable rates of transformation, the nucleation rate should be high enough so that a small number of nuclei (say C) must appear in a short period of time (say 1 sec). Then,

$$R \times \text{particle volume} = C$$

or

$$R \times \frac{4\pi r^3}{3} = C$$

where r is the particle radius.

or

$$\frac{1}{r^3} = \frac{4\pi R}{3C} = \left(\frac{4\pi R_0}{3C}\right) \exp(- A f(\theta)\, \gamma^3/\Delta T^2), \qquad (2)$$

or

$$-3 \ln \langle r \rangle = \ln \left(\frac{4\pi R_0}{3C}\right) - A f(\theta)\, \gamma^3/\Delta T^2, \qquad (3)$$

or

$$\ln \langle r \rangle = B + C\gamma^3/\Delta T^2, \qquad (4)$$

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where

$$C = 16\pi T_0\, f(\theta)/9kT\,(\Delta H_V)^2\,. \qquad (5)$$

If $f(\theta)$ is taken as 1 in equation 3 the interfacial energy, γ, can be evaluated from the linear plots of $\ln \langle r \rangle$ against $1/\Delta T^2$. Such linear plots have been reported by Natarajan, Das and Rao [3].

3. γ from (DTA) Transformation Curves

Considering a pair of reversible transformation curves obtainable from a DTA experiment (fig. 1) the ordinate Y which represents the transformation rate can be considered proportional to R in equation 1. Although the absolute values of R change very rapidly with ΔT when transformation proceeds, still the ordinate Y can be considered proportional to R, so that,

$$Y = KR = KR_0 \exp\{-A\gamma^3/\Delta T^2\}\,, \qquad (6)$$

where K is unknown but may have a very small value. If equation 6 is valid, a plot of $\ln Y$ versus $1/\Delta T^2$ (fig. 2) will give a measure of γ from the slope. The unknown proportionality constant K will not affect the values of γ thus evaluated.

4. γ by Calculations from Crystal Structures

Bruce [5] has made theoretical estimates of change in surface free energy in solid-liquid and solid-vapour transformations for a number of inorganic crystalline materials. For the solid-liquid transformation, Bruce employs the relation,

$$\gamma = \left(\frac{B}{A}\right) \Delta H_{\mathrm{T}} \left(\frac{J}{N}\right) \qquad (7)$$

where γ is the change in surface free energy and may be taken as equal to the interfacial energy, B is the ratio of "free" bonds to total co-ordination bonds per atom/molecule on the surface, $1/A$ is the number of atoms per unit area of the interface, ΔH_{T} is the gram atomic heat of transformation, N is the Avogadro number, and J is the Joule constant. If this can be extended to the solid-solid transformation going from α- to β-phase, so that the term B/A may now be written as the average difference between the free bonds per unit area of the transforming interface, then,

$$\frac{B}{A_{(\mathrm{average})}} = \frac{B}{A_\alpha}\,(\alpha\text{-phase}) - \frac{B}{A_\beta}\,(\beta\text{-phase})\,, \quad (7)$$

where both the values on the right-hand side of equation 7 are taken for lowest B/A values corresponding to the surfaces of lowest energy for the particular structure. Equation 7 can now be written as,

$$\gamma = \frac{B}{A_{(\mathrm{average})}}\,\Delta H_{\mathrm{T}}\,\frac{J}{N}\,. \qquad (8)$$

The $B/A_{(\mathrm{average})}$ can be evaluated, for example, for CsCl, Pm3m ⇌ Fm3m transformation. In the fcc structure, the B/A value is the least for the (100) face:

area of the face $= a_1^2$, where a_1 is the lattice constant;

number of ions on this face = 4(2 cations + 2 anions);

value of B, the ratio of free bonds to total co-ordination bonds on (100) face = 1/6.

Therefore $1/A = 4/a_1^2$ and $B/A = 2/3\, a_1^2$. For the bcc structure the (110) face has the least value for B/A so that the area $= \sqrt{2}\, a_2^2$ where a_2 is the lattice constant. The number of ions in this area is 2 (cations or anions) and $1/A = 2\sqrt{2}\, a_2^2$. The value of B can be seen to be $\frac{2}{8} = \frac{1}{4}$. Therefore $B/A = 1/2\sqrt{2}\, a_2^2$. Hence the interfacial energy γ is given by equation 8.

$$\gamma = \frac{B}{A_{(\mathrm{average})}}\,\Delta H_{\mathrm{T}}\,\frac{J}{N}$$

$$= \left(\frac{2}{3}\,a_1^2 - \frac{1}{2}\,\sqrt{2}\,a_2^2\right) \frac{300 \times 4.2 \times 10^7}{10^{-16} \times 6.023 \times 10^{23}}$$

$$= 1.5 \text{ ergs cm}^{-2}\,,$$

where $a_1 = 4.1210$ Å, $a_2 = 6.9100$ Å, and $\Delta H_{\mathrm{T}} = 300$ cal g ion^{-1} (from DTA curves) [3].

5. Results and Discussion

The calculated values for the interfacial energies are furnished in table I, along with the values of γ obtained from particle size variation (equation 4) and DTA curves (equation 6). The Bruce method of calculation does not seem to be applicable to the α ⇌ β quartz transformation which is a displacive transformation where both the phase structures are similar, the α-phase being a slightly distorted version of β, the higher temperature phase. Due to the hygroscopic nature of the halides, which made separation of particles in the micron range very difficult, the analysis of the particle size effects could not be extended to these materials.

5.1. Analysis of DTA Curves

The analysis of the DTA transformation curves on the basis of equation 6, yielded values of γ that are listed in table I. The plot of $\ln \gamma$ versus

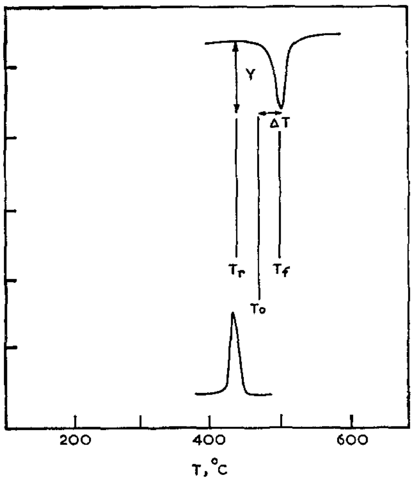

Figure 1 Typical DTA transformation curves for CsCl; T_f, forward transformation temperature; T_r, reverse transformation temperature; T_0, equilibrium transformation temperature.

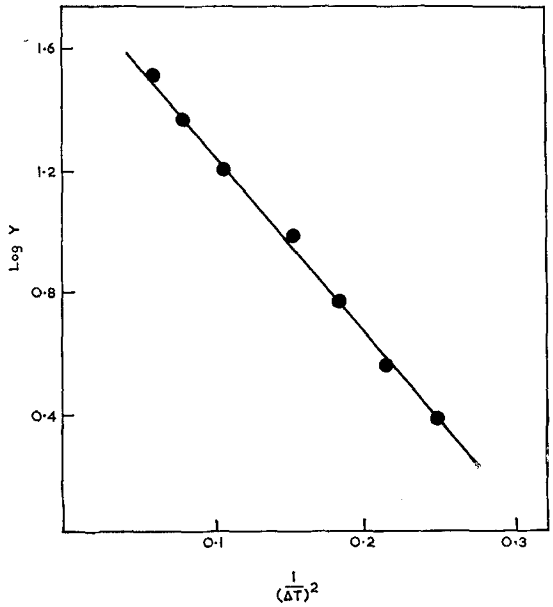

Figure 2 Plot of log γ versus $1/(\Delta T)^2$ for CsCl transformation.

$1/\Delta T^2$ for CsCl is shown in fig. 2. The ΔH_T values employed for the calculation of γ, are listed in table I.

Considering (*a*) the simplicity of the assumptions implicit in the theoretical calculations of γ, (*b*) the assumption that $f(\theta) = 1$ in equation 5 and (*c*) taking the ordinate γ of DTA curves (fig. 1) to be proportional to the nucleation rate, *R*, the agreement of values of γ by the three methods outlined in this investigation is fairly satisfactory. The slightly large differences in the γ-values, in the case of AgI, may be attributable to the uncertainty of the cation positions in the high temperature phase, which are considered to be random and fluid.

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TABLE I Interfacial energies, γ (ergs cm^{-2}), of some solids

Solids	Transformation studied	ΔH_T cal g ion^{-1}	γ from particle size (equation 4)	γ from DTA curves (equation 6)	γ from Bruce's method (equation 8)
Quartz	α-β inversion	50	1.3	1.0	—
K_2SO_4	orthorhombic $\rightleftharpoons$ hexagonal	1070	1.4	—	—
CsCl	Pm3m $\rightleftharpoons$ Fm3m	300	—	0.9	1.5
NH_4Cl	Pm3m $\rightleftharpoons$ Fm3m	550	—	2.0	3.4
NH_4Br	Pm3m $\rightleftharpoons$ Fm3m	450	—	1.5	1.6
AgI	hexagonal cubic	800	—	4.4	1.6