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Prediction of thermodynamic properties for multicomponent system with Chou model①

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[Abstract] A new geometrical model, Chou model, was developed as a computer program for calculating thermodynamic properties of multicomponent system. Calculated results show that the new model is more reasonable and convenient than other symmetrical (or asymmetrical) models. With this model, the excess Gibbs free energies of Ga-Al-As-In compound semiconductor system were calculated.

[Key words] thermodynamic properties; new geometrical model; Ga-Al-As-In alloy
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1 INTRODUCTION

The group III-V compound semiconductors and their solid solutions are important materials for photoelectronic and high speed electronic applications. The fabrication of these components involves many complex processes. For example, the solid and liquid phases coexist at near equilibrium condition including crystal growth and liquid phase epitaxy, the solid and vapour phases coexist including chemical vapour deposition. Therefore, the phase diagram and thermodynamic properties for these systems are important for providing boundary condition in analysis of processes.

Though databases were previously published and additional experimental measurements were reported for many systems to modify the conclusions of the previous databases, it is still not enough. Because different models and reference states are used, it is difficult to supply systematically thermodynamic data for multicomponents.

Recently, Chou[1] established a new geometric model for calculating the thermodynamic properties of liquid multicomponent systems. It overcomes the defects of previous traditional geometric models[2,3]. And it is expected to apply in some liquid multicomponent systems, in which it is difficult to select symmetrical (or asymmetrical) geometric model and asymmetrical component. In this article, the new geometric model was applied in prediction for the thermodynamic properties of Ga-Al-As-In compound semiconductor system. And the results were compared with that of previous typical geometrical models.

2 CHOU MODEL

Firstly, a quantity $\eta_{(ij,ik)}$ is defined as deviation sum of squares:

$$\eta_{(ij,ik)} = \int_0^1 (\Delta G^E_{ij} - \Delta G^E_{ik})^2 \mathrm{d}X_{i(ij)} \quad (1)$$

where ΔG^E_{ij} and ΔG^E_{ik} represent the excess Gibbs free energies of binary systems i-j and i-k, respectively; $X_{i(ij)}$ indicates the mole fraction of component i in i-j.

Then another quantity $\xi^k_{(ij)}$, similarity coefficient, is introduced, which is defined as

$$\xi^k_{(ij)} = \frac{\eta_{(ij,ik)}}{\eta_{(ij,ik)} + \eta_{(ji,jk)}} \quad (2)$$

On basis of the above definition, the following binary compositions are selected for this new model:

$$X_{i(ij)} = x_i + \sum_{\substack{k=1 \\ k\neq i,j}}^{n} x_k \xi^k_{(ij)} \quad (3)$$

where x_i and x_k denote the mole fractions of components i and k in a multicomponent system, respectively.

This new model differs from other geometrical models in its special selection of binary compositions that are of close relation with the multicomponent system considered. For instance, the selection of binary composition in i-j system depends on the characteristics of systems k-i and j-k in a i-j-k ternary system. The coefficient $\xi^k_{(ij)}$, which expresses the symmetrical characteristics of components quantitatively, represents similarity of k with i and j. When two components are exactly same in a ternary system, the ternary system will become a binary one with this model, it overcomes the defect of symmetrical geometric models.

In multicomponent system, ΔG^E_{ij} is expressed as the following Ridlich-Kister[4] multinominal:

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$$\Delta G_{ij}^{E} = X_{i(ij)} X_{j(ij)} \sum_{v}^{n} L_{ij}^{v} [X_{i(ij)} - X_{j(ij)}]^{v} \quad (4)$$

where $X_{j(ij)}$ denotes mole fraction of component j in the binary i-j. L_{ij}^{v} represents the interaction parameter for binary i-j, which is independent of compositions but dependent on temperature.

Combining Eqns.(1) ~ (4), the excess Gibbs free energy ΔG^{E} can be obtained for a multicomponent system from relative binaries:

$$\Delta G^{E} = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{x_i x_j}{X_{i(ij)} X_{j(ij)}} \Delta G_{ij}^{E} \quad (5)$$

3 RESULTS AND DISCUSSION

The new model (Chou model), other symmetrical and asymmetrical models were developed as computer application program, the mixing molar Gibbs free energies for the asymmetrical system Ag-Sn-Zn (Ag as the asymmetrical component) at 900 K are calculated, as shown in Fig.1. For comparison, the results of some typical symmetrical models (Kohler, Colinet, Muggianu)[5~7] or asymmetrical model (Toop model)[8] as well as the experimental data are also included. From the results, it can be seen that the calculated data from new model is much more similar to the experimental data[9] than those predicted by other models.

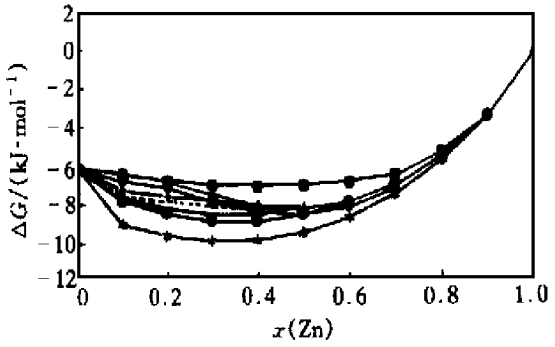

Fig.1 Comparison between measured and calculated molar Gibbs free energies in ternary Ag-Sn-Zn (Ag/Sn=1)
—New model; ▼—Kohler model; + —Colinet model; ▲—Muggianu model; ■—Toop model(Sn as asymmetrical component); * —Toop model(Zn as asymmetrical component); ---Toop model(Ag as asymmetrical component); ●—Experimental data

In multicomponent Ga-Al-As-In system, the molar excess Gibbs free energies of all sub-binaries in this system at 2100 K are shown in Fig.2. The similarity coefficients for all sub-binaries in this system at 2100 K are shown in Table 1. And the molar excess Gibbs free energies of liquid Ga-Al-As-In four component system were calculated, as shown in Fig.3.

By comparing the molar excess Gibbs free energies of its sub-binaries at 2100 K, it can be seen that Al-As-Ga-In system is an asymmetrical one. So the asymmetrical model should be used rather than the symmetrical one. But it is not clear which component is the asymmetrical one. From Fig.3, when As or In acts as the asymmetrical component in this case meet the new model very well, and when Ga or Al acts as the asymmetrical component will lead to deviation due to the wrong selection for asymmetrical component.

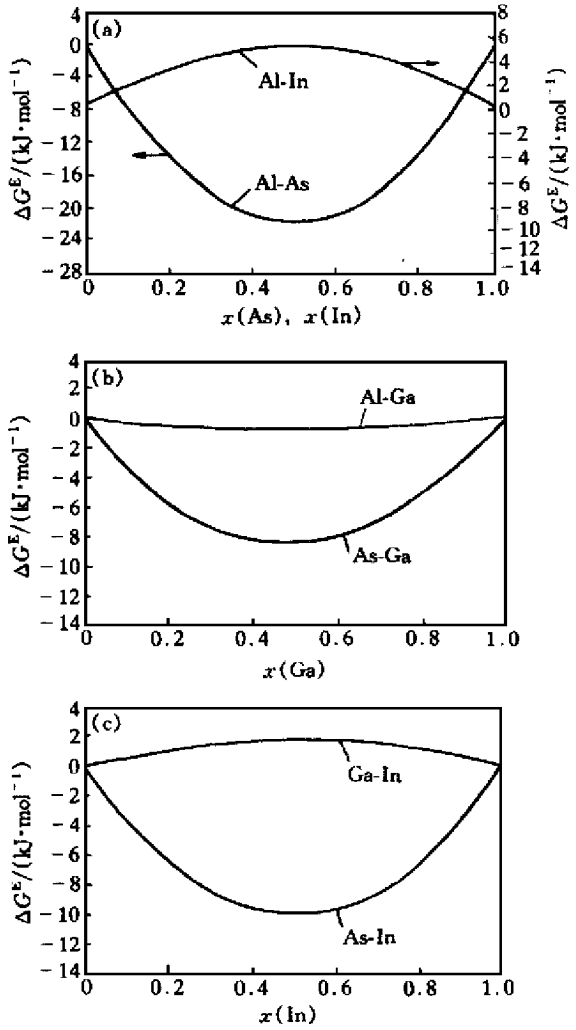

Fig.2 Comparison of excess Gibbs free energies of sub-binaries in Al-As-Ga-In system at 2100 K
(a)—Al-As, Al-In; (b)—Al-Ga, As-Ga; (c)—As-In, Ga-In

Obviously, it is very important to select an appropriate model or asymmetrical component in calculation. For those systems whose symmetry is not obvious, neither symmetrical model or asymmetrical model can meet the condition. The new model properly indicates the relationship of the components in systems by using similarity coefficient and can be used in most of practical systems than symmetric or asymmetric models do.

Table 1 Similarity coefficient in Al-As-Ga-In system at 2100 K

Similarity coefficient	Al-As-Ga-In(1-2-3-4)	As-Ga-In-Al(1-2-3-4)	Ga-In-Al-As(1-2-3-4)	In-Al-As-Ga(1-2-3-4)
ξ_{2-3}	0.71547	0.01532	0.38981	0.23507
ξ_{2-4}	0.83511	0.74320	0.44416	0.23613
ξ_{3-2}	0.87919	0.01228	0.16491	0.60734
ξ_{3-4}	0.83893	0.39226	0.12081	0.98772
ξ_{4-2}	0.76403	0.28453	0.98468	0.61019
ξ_{4-3}	0.75982	0.16575	0.25680	0.55584
ξ_{3-1}	0.74320	0.44416	0.23613	0.83425
ξ_{3-4}	0.01532	0.38981	0.23507	0.71547
ξ_{4-1}	0.38998	0.12081	0.98772	0.83509
ξ_{4-3}	0.01228	0.16491	0.60734	0.87919
ξ_{4-1}	0.37788	0.23507	0.71547	0.01532
ξ_{4-2}	0.44416	0.23613	0.83425	0.74320

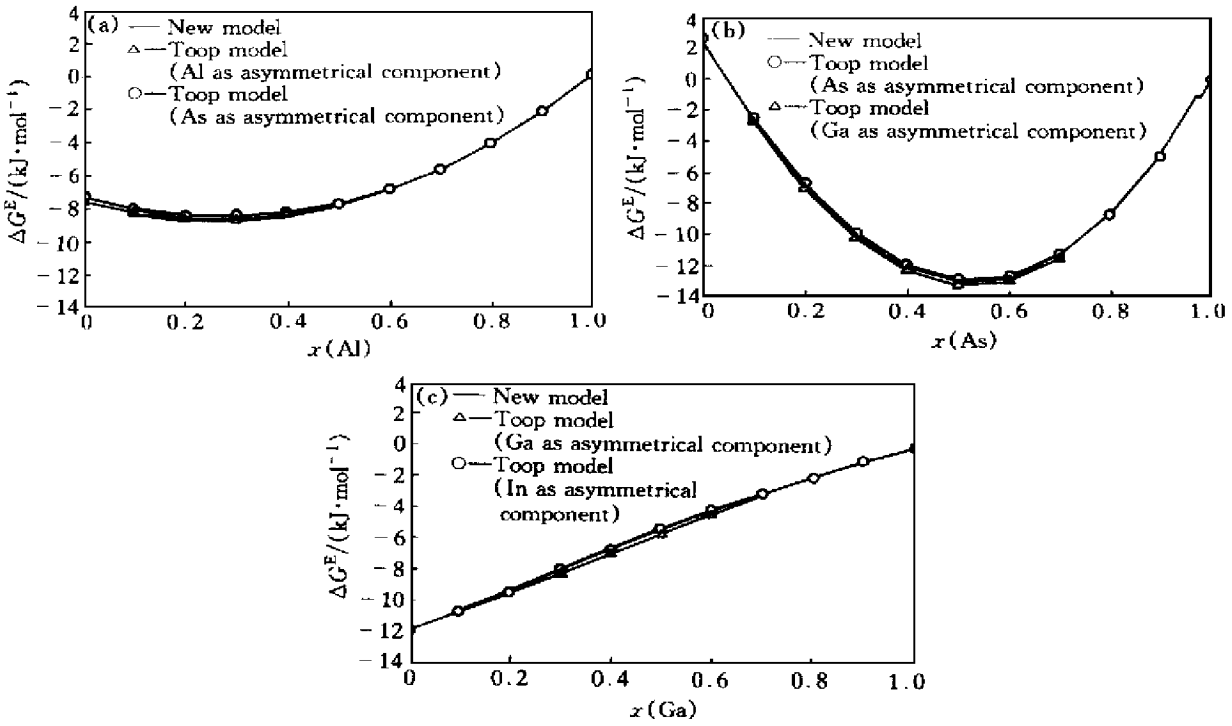

Fig.3 Excess Gibbs free energies of Ga-Al-As-In system at 2100 K
(a) — x(As) = x(Ga) = x(In); (b) — x(Ga) = x(In) = x(Al); (c) — x(In) = x(Al) = x(As)

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