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Thermodynamic and Transport Properties of Liquid Gallium

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액체 갈륨의 열역학적 및 수송학적 성질에 관한 연구

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Abstract

The significant structure theory of liquids has been successfully applied to liquid gallium. In this work, we have assumed that two structures exist simultaneously in liquid gallium. One is considered as loosely close packed β-Ga-like structure and the other is the remainder of solid α-Ga or α-Ga-like structure. This two structural model is introduced to construct the liquid partition function. Using the partition function, the thermodynamic and transport properties are calculated over a wide temperature range. The calculated results are quite satisfactory when compared with the experimental results.

요 약

액체특성구조이론을 액체 갈륨의 구조와 성질연구에 적용하였다. 이 연구에서 액체 Ga 속에는 β-Ga와 비슷한 구조와 α-Ga와 비슷한 구조의 두가지가 있다는 가정을 하여 액체분배함수를 구하였다. 이를 사용하여 넓은 온도 범위에서 액체 Ga의 열역학적 및 수송학적 성질을 구하였다. 계산결과는 실험치와 잘 일치함을 보여주고 있다.

I. Introduction

Gallium is a metal which is characterized by some peculiar properties.[1~3] The most unique features are its long liquid range from a supercooled state of at least 150°K[4] to the boiling point of 2510°K, and the low vapor pressures even at high temperatures. It is also noteworthy that gallium shows the anomalous density increase of 3.2% upon melting, whereas most of metals show a density decrease of 2-6%.

In this work we applied the significant structure theory to liquid gallium. This theory was first applied to liquid metals by Carlson, Eyring and Ree.[5] Considering an equilibrium between monomers and dimers in the gas phase, Breitling and Eyring[6] calculated thermodynamic and

transport properties of many liquid metals, but their results were not satisfactory. Hsu et al.[7] could obtain better results for thermodynamic properties of alkali metals by taking account of the volume dependences of sublimation energy and Einstein characteristic temperature.

In general, liquid metals are considered as being monatomic simple liquids. However many experiments have shown that the liquid gallium has its own particular structure which is different from those of simple liquids. Thus we must take into accunt the structure of liquid gallium to derive a liquid partition function correctly by which all thermodynamic and transport properties can be calculated.

II. Structural Model of Liquid Gallium

There have been a number of studies on the structure of liquid gallium, and several structural models were proposed. Ascarelli[8] proposed that the structure of liquid gallium is similar to the structure of metastable β-Ga. Comparison with the crystalline phase showed that the atomic distribution in the liquid more resembles the metastable β phase than the stable α phase. The Knight shift measurements also showed the close similarity between β-Ga and liquid gallium.[9] The metastable β-Ga is formed when the liquid is supercooled. The melting behavior of β-Ga is much more normal compared to that of α-Ga, at least as far as the changes in density and in electrical resistivity are concerned. And it is known that the structure of supercooled liquid gallium does not differ significantly from that of normal liquid gallium.[10] Thus the metastable β-Ga can be considered as the parent solid of the liquid gallium. A quasicrystalline model related to β-Ga was also proposed by Bizid et al.[11] in order to explain the shape of the structure factor of liquid gallium.

On the other hand, the possibility of the persistence of the diatomic grouping found in solid α-Ga into the liquid state has been widely discussed. X-rays and neutron diffraction measurements reveal a shoulder on the high angle side of the main peak in the structure factor of liquid gallium, and the shoulder weakens as temperature increases. Rodriguez and Pings[10] proposed that it is due to the existence of Ga-Ga pairs in the liquid, as in the solid α-Ga. If it is so, the order of the solid α-Ga may be to a certain degree preserved as the solid melts, as suggested by Pokorny and Aström[12] in terms of 'after melting effect'. This effect represents the continuation of the melting process far into the liquid region.

Thus it seems reasonable to assume a model in which two structures are exist in liquid gallium. Orton[13] proposed a double hard sphere model to reproduce the strucure factor of supercooled liquid gallium. Richter[14] also proposed that in liquid gallium two structures exist simultaneously, i.e., the layer lattice structure and the spherical close packing in the form of a straight atomic chain. According to him, the layer lattice structure is the remainder of the solid α-Ga, and its contribution is small. From the analysis of the radial distribution curves, Romanova and Mel'nik[15] proposed a model that liquid gallium contains micro-regions with the peculiar structure of solid α-Ga and micro-regions with a short-range order in which the minimum distance and coordination number are greater than those in the solid structure. The proportion of the first type of micro-regions is small, and decreases as temperature increases.

Considering the facts mentioned, we can give the following qualitative description for the structure of liquid gallium. The melting of solid is accompanied by alterations in its structure as well as introduction of fluidized vacancies. Upon melting, most of solid structure deforms

into a denser form, β-Ga-like structure. It is similar to the structure of metastable β-Ga in a short-range order, but on the whole it is more analogous to the loosely close packing structure of simple liquid. The remainder is preserved as the solid melts. This α-Ga-like structure has the characteristic short-range order of solid α-Ga. Atoms which constitute α-Ga-like structure are dispersed in atoms of β-Ga-like structure, and an equilibrium is established between atoms of two structures. As temperature increases, α-Ga-like structure is transformed into β-Ga-like structure, which resembles more and more the structure of simple liquid like liquid argon. Considering this structural model we write down a partition function for liquid gallium.

III. Formulations of Partition Function

According to the significant structure theory[16], the partition function for a liquid, f_N, is given by

$$f_N=\left[f_s\left\{1+n\frac{V-V_s}{V_s}e^{-aE_s V_s/(V-V_s)RT}\right\}\right]^{NV_s/V}\cdot f_g^{N(V-V_s)/V} \quad [1]$$

Here, the notations in Eq. [1] have the usual statistical mechanical significance or will define later.

Since we have assumed that there are two structures in equilibrium,

$$\beta\text{-Ga-like}\underset{}{\overset{K}{\rightleftharpoons}}\alpha\text{-Ga-like}$$

the equilibrium constant, K, is written as

$$K=[\alpha\text{-Ga-like}]/[\beta\text{-Ga-like}]=f_\alpha/f_\beta=\exp\left[\frac{-\Delta H+T\Delta S-P\Delta V}{RT}\right] \quad [2]$$

Thus the solid-like partition function, f_s, is

$$f_s^{NV_s/V}=f_\alpha^{N\alpha}\cdot f_\beta^{N\beta}=f_\beta^{NV_s/V}(f_\alpha/f_\beta)^{N\alpha}=(f_\beta K^{K/1+K})^{NV_s/V} \quad [3]$$

where N_α and N_β are the number of α-Ga-like atoms and that of β-Ga-like atoms, respectively. The β-Ga-like structure has been considered as loosely close packing, so that the solid-like partition function of simple liquid can be used for the β-Ga-like partition function f_β, i.e.,

$$f_\beta=\frac{e^{E_s/RT}}{(1-e^{-\theta/T})^3} \quad [4]$$

From a mass spectrometric study[17], the vapor of liquid gallium is considered as being monatomic. So the gas-like partition function, f_g, is written as

$$f_g=\frac{(2\pi mkT)^{3/2}}{h^3}\cdot\frac{eV}{N} \quad [5]$$

Thus the overall partition function of liquid gallium is

$$f_N=\left[\frac{e^{E_s/RT}}{(1-e^{-\theta/T})^3}\left\{1+n\cdot\frac{V-V_s}{V_s}\times e^{-aE_sV_s/(V-V_s)RT}\right\}K^{K/1+K}\right]^{NV_s/V}\cdot\left[\frac{(2\pi mkT)^{3/2}}{h^3}\cdot\frac{eV}{N}\right]^{N(V-V_s)/V} \quad [6]$$

In the calculations the solid-like molar volume, V_s, is given by

$$V_s=\frac{K}{1+K}V_\alpha+\frac{1}{1+K}V_\beta \quad [7]$$

Here the solid-like molar volumes V_α and V_β are assumed to be temperature dependent, i.e.,

$$V_\alpha=V_{\alpha 0}(1+AT) \quad [8]$$

$$V_\beta=V_{\beta 0}(1+B_1T+B_2T^2) \quad [9]$$

Where A and B are thermal expansion coefficient of α-Ga-like and those of β-Ga-like, respectively; the second term B_2 in Eq.[9] is introduced to obtain better thermodynamic properties. In accord with previous experience with molten metals[7], the volume dependences of sublimation energy, E_s and Einstein characteristic temperature, θ are introduced as follows

$$E_s=E_{s0}\{2(V_{\beta 0}/V_\beta)^q-(V_{\beta 0}/V_\beta)^{2q}\} \quad [10]$$

$$\theta=\theta_0(V_{\beta 0}/V_\beta)^\gamma \quad [11]$$

where subscript zero means absolute zero; q is a parameter and γ is Grüneisen's constant.

IV. Results and Discussion

The Helmholtz free energy, A, is related to

the partition function by $A=-kT \ln f_N$. The molar volume and vapor pressure are found from the tangent to a plot of the Helmholtz free energy against volume.[18] The points of tangency are the liquid and vapor molar volumes and the slope of the tangent is the vapor pressure since $P=-(\partial A/\partial V)_T$.

To determine the parameters in the partition function, we used modified Seoul technique[19] which has been applied to liquid water whose structural model is similar to our model for liquid gallium. Parameters which could not evaluated by this method were taken to give the best results. The parametric values used in the calculations are given in Table 1. All the liquid properties were calculated from 400°K to the boiling point at 100° increments.

Table 1. Parameters Used in Calculations

$E_{s0}=56.54$kcal/mole	$a=4.96\times10^{-6}$
$\theta_0=101.8$°K	$n=80$
$V_{\alpha0}=11.20$cm^3/mole	$\Delta H=-1.59$kcal/mole
$V_{\beta0}=11.25$cm^3/mole	$\Delta S=-8.20$e.u.
$A=1.0\times10^{-4}$°K^{-1}	$q=1.13$
$B_1=0.71\times10^{-4}$°K^{-1}	$\gamma=2.2$
$B_2=-0.14\times10^{-7}$°K^{-1}	

1) Vapor Pressure and Molar Volume

The calculated values of vapor pressure are compared with the selected values of Hultgren et al.[20] as shown in Fig. 1. All experimental measurements were made between 1,000°K and 1,400°K. The experimental values[21] are not shown, but these values agree well with the selected values. The calculated boiling point is 2,616.6°K, which is comparable to the selected value of 2,510°K. Fig. 2 shows the calculated and experimental values[22] of molar volume.

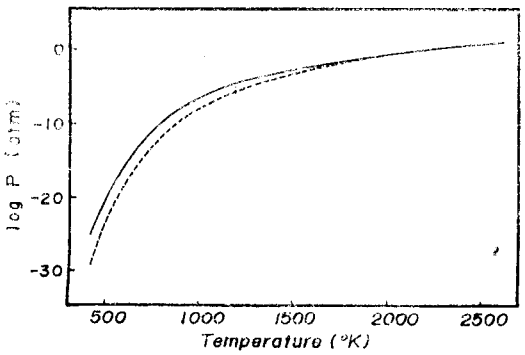

Fig. 1. Vapor Pressure of Liquid Gallium —, Calculated; ···, Selected[20]

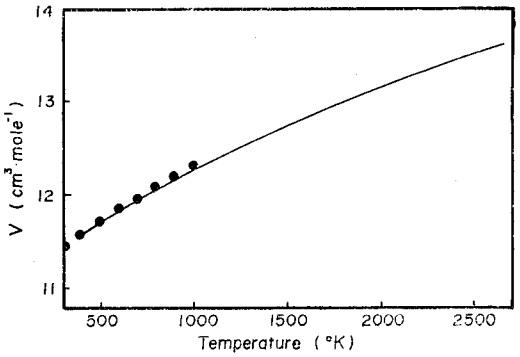

Fig. 2. Molar Volume of Liquid Gallium —, Calculated; ●, Experimental[22]

2) Thermal Expansion Coefficient and Compressibility

For simple liquids the increase in volume is mainly due to the introduction of fluidized vacancies. But in the case of liquid gallium, the change in solid-like volume over a wide temperature range cannot be ignored. Thus we must take into account the contribution of solid-like structure on thermal expansion coefficient and compressibility, i.e.,

$$\alpha=\alpha_f+\frac{V_s}{V}(\alpha_{\beta\text{-Ga}}+\alpha_{st}) \quad [12]$$

$$\beta=\beta_f+\frac{V_s}{V}(\beta_{\beta\text{-Ga}}+\beta_{st}) \quad [13]$$

The values contributed by fluidized vacancies, α_f and β_f, are calculated from the partition function.

$$\alpha_f=\frac{1}{V}\left(\frac{\partial^2 \ln f_N}{\partial V \partial T}\right)\Big/\left(\frac{\partial^2 \ln f_N}{\partial V^2}\right)_T \quad [14]$$

$$\beta_f=-\frac{1}{V}\Big/kT\left(\frac{\partial^2 \ln f_N}{\partial V^2}\right)_T \quad [15]$$

The values contributed by the β-Ga-like structure, $\alpha_{\beta\text{-Ga}}$ and $\beta_{\text{-Ga}}$, are calculated from the β-Ga-like partition function. Also the values

contributed by structural change from β-Ga-like to α-Ga-like structure, α_{st} and β_{st}, are calculated as follows,

$$\alpha_{st}=\frac{1}{V_s}\left(\frac{\partial V_s}{\partial T}\right)_P = \frac{1}{V_s}\left(\frac{\partial K}{\partial T}\right)_P \Big/ \left(\frac{\partial K}{\partial V_s}\right)_P \quad [16]$$

$$\beta_{st}=-\frac{1}{V_s}\left(\frac{\partial V_s}{\partial P}\right)_T = -\frac{1}{V_s}\left(\frac{\partial K}{\partial P}\right)_T \Big/ \left(\frac{\partial K}{\partial V_s}\right)_T \quad [17]$$

Thermal expansion coefficient of liquid gallium exhibits a decreasing function of temperature. The calculated values are in good agreements with the experimental values quantitatively as well as qualitatively. This comparison is shown in Fig. 3. The calculated compressibility is shown in Fig. 4, and compared with the experimental value.

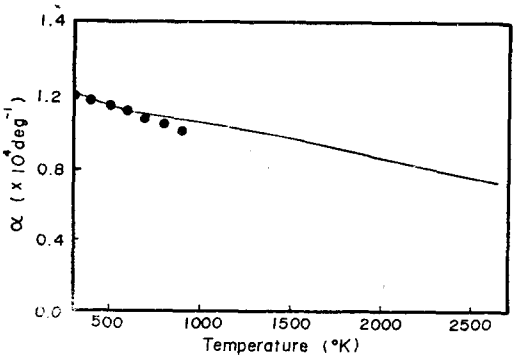

Fig. 3. Thermal Expansion Coefficeint of Liquid Gallium.
—, Calculated, ●, Experimental[22]

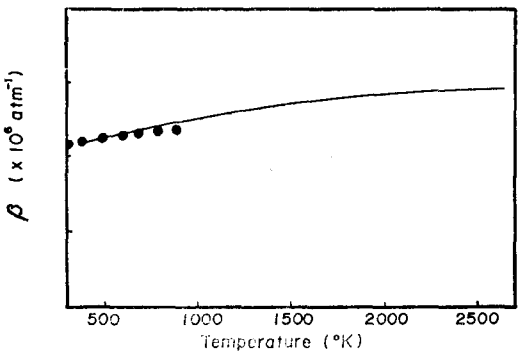

Fig. 4. Compressibility of Liquid Gallium
—, Calculated; ●, Experimental[22]

3) **Entropy and Heat Capacity**

The entropy is calculated by using the equation

$$S=\frac{\partial}{\partial T}(kT\ln f_N)_V \quad [18]$$

The calculated values are shown in Fig. 5 and compared with the selected values of Hultgren et al.

Heat capacities at constant volume, C_V, and those at constant pressure, C_P, are also calculated by using the following thermodynamic relations

$$C_V=\left[\frac{\partial}{\partial T}\left\{kT^2\left(\frac{\partial \ln f_N}{\partial T}\right)_V\right\}\right]_V \quad [19]$$

$$C_P=C_V+TV\alpha^2/\beta \quad [20]$$

The measurements of heat capacity showed that C_V and C_P are decreasing functions of temperature[23], and the values at high temperature are

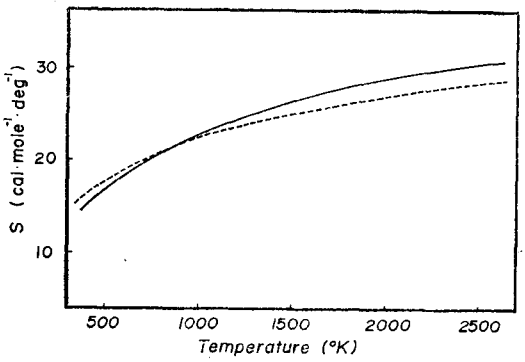

Fig. 5. Entropy of Liquid Gallium.
—, Calculated; ···, Selected[20]

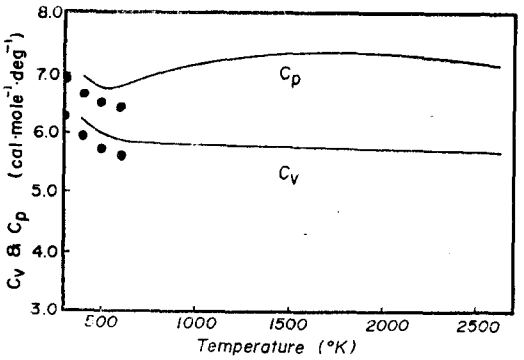

Fig. 6. Heat Capacity of Liquid Gallium.
—, Calculated; ●, Experimental[23]

expected to be nearly constant. Fig. 6 shows the calculated and experimental values of heat capacities. The large deviation in C_P from the expectation may be due to the errors in the calculated values of α and β.

4) Viscosity and Self-Diffnsion Coefficient

According to the significant structure theory[17] the viscosity equation can be deduced as follows

$$\eta=\frac{Nh}{z\kappa}\ \frac{6}{\sqrt{2}}\ \frac{1}{1-e^{\theta/T}}\ \frac{1}{V-V_s}\ \exp\left\{\frac{a'E_sV_s}{(V-V_s)RT}\right\}+\frac{V-V_s}{V}\ \frac{2}{3d^2}\left(\frac{mkT}{\pi^3}\right)^{1/2} \quad [21]$$

In calculations, the transmission coefficient, κ, is taken as 0.997 and the proportionality constant, a', as 1.0×10^{-6}. The calculated and experimental values[24~25] of viscosity are shown in Fig. 7. At low temperatures the calculated values are somewhat higher than the experimental values. But at high temperatures the agreement is quite satisfactory. It is found that the contribution of gas-like atoms is negligible, because it is within 1% in total at whole temperature range.

The self-diffusion coefficient, D, is given by

$$D=\frac{kT}{6\left(\frac{\sqrt{2}V_s}{N}\right)^{1/3}\eta} \quad [22]$$

The calculated results are compared with the experimental ones[26] in Fig. 8. Experimental

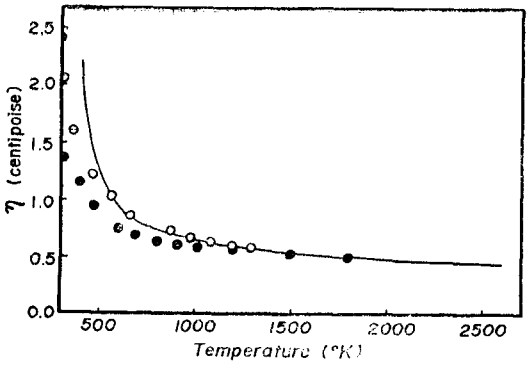

Fig. 7. Viscosity of Liquid Gallium. —, Calculated; ○, Experimental[24] ●, Experimental[25]

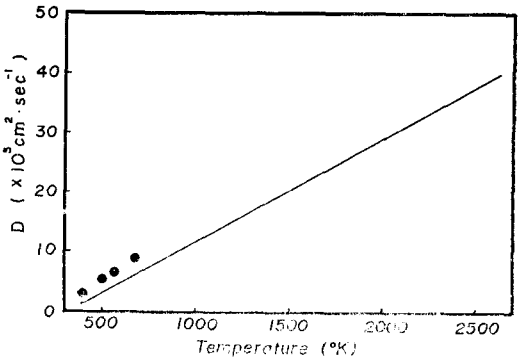

Fig. 8. Self-diffusion Coefficient of Liquid Umgalli —, Calculated; ●, Experimental[26]

values at high temperatures are not available. However the self-diffusion coefficient is directly related to the viscosity, so that the calculated values at high temperature are considered to agree well with real values.

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