Vol 12 No 3, March 2003
1009-1963/2003/12(03)/0315-07
Chinese Physics
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Surface behaviour and undercooling in the liquid Ga-Bi binary system detected by optical second harmonic generation*

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(Received 27 May 2002; revised manuscript received 19 December 2002)

We employ an optical second harmonic generation(SHG) technique to investigate the surface behaviours at the liquid(solid)/vapour interface of the Ga-Bi binary metallic system. In a heating and cooling cycle between 280°C and room temperature, there is no change of the SH-intensity in the heating process, whereas there exists an abrupt and abnormal change of the SH-intensity in the cooling process. It is interesting to find that a macroscopic Bi-rich solid layer is floating on the surface of the Ga-rich liquid phase just below the monotectic temperature (222°C±2°C) in the cooling process, in spite of the Bi-rich phase being heavier than the Ga-rich phase. On the other hand, different undercooling behaviours are observed at the surface and in the bulk. The behaviours of surface solidification and surface melting are different from those in the bulk.

Keywords: surface phase transition, second harmonic generation liquid(solid)/vapour interface, Ga-Bi binary alloy, undercooling

PACC: 6842, 6470D, 4265, 6125M

1. Introduction

Interfacial study is an important subject in physics and chemistry of condensed matter. Interfacial phase transitions, especially the wetting phenomena, attract a great deal of theoretical and experimental investigations[1,2] since Cahn's paper published in 1977.[3] But most experiments focused on the organic systems with van der Waals interactions. More recently, it is interesting to find that Coulomb liquids like liquid binary alloys or metal molten salt solutions also exhibit wetting transition. Nattland and Freyland[4] reported the first observations of a wetting transition in K-KCl system. References [5] and [6] were on Cs-CsCl, Rb-RbCl and Na-NaCl. Using second harmonic generation(SHG) Tostmann *et al*[7] reported for the first time the wetting and prewetting transitions at solid/liquid interface of K-KCl system. Especially, Nattland and coworkers,[8−10] Wang *et al*[11] and Turchanin *et al*[12] reported their experimental results on surface phase transitions and the wetting phenomena at the liquid/vapour interface of Ga-Bi system by spectroscopic ellipsometry, SHG technique and plasma excitation. Chatain and Wynblatt[13,14] reported the study of the wetting transition at the liquid/vapour interface of Ga-Pb binary liquid alloy using Auger electron spectroscopy. Rice and co-workers[15−17] and Pershan and co-workers[18,19] carried out much research on the longitudinal density distribution and transverse structure at the liquid–vapour interface of pure metals and dilute alloys like Ga, Mg, Ga-Bi, Ga-Sn Ga-Ln by grazing incidence x-ray diffraction or x-ray reflectivity. They found that there exists a Gibbs adsorbate monolayer or submonolayer of pure Bi at the liquid/vapour interface of Ga-Bi dilute alloys. Unfortunately, few experiment were concerned with the surface phase transitions with the variation of temperature and composition.

Liquid metal and alloy interfaces play an important role in many technologies: from the basic metal production processes, like smelting and refining, to the complicated metal forming processes, like zone melting, casting and brazing. Details of the temperature dependence of the processes, especially at the liquid–vapour interfaces are still poorly understood.

On the other hand, second-order nonlinear opti-

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cal techniques, such as SHG, have been developed as extremely versatile and sensitive surface and interface probes over the past years.[20−23] SHG is forbidden in the bulk with an inversion symmetry under the electric dipole approximation, because the second-order bulk susceptibility $\chi^{(2)}$ vanishes under inversion symmetry. However, the inversion symmetry is necessarily broken at the interface. So SHG is intrinsically sensitive to the interfacial region with a thickness of monolayer.

A wetting phenomenon at the liquid (solid) /vapour interface of the Ga-Bi binary metallic system means that a macroscopic layer of a more dense liquid (or solid) Bi-rich phase (ρ_{Bi}=9.8g/cm^3) is able to overcome gravity and resides on the top of a less dense liquid Ga-rich phase (ρ_{Ga}=5.9g/cm^3), due to its favourable liquid(solid)/vapour interfacial tension. This phenomenon results from the competition of the Coulomb interaction and gravity. At the liquid/vapour interface in the Ga-Bi system, wetting transition is concerned with a surface component transition from the Ga-rich phase to the Bi-rich film phase. The intensity and polarization properties of the second harmonic light beam are measured in reflection as a function of temperature and composition. The information about the interface can be included in the surface nonlinear susceptibility tensor.

The focus of this work is the in situ measurement of the surface phase transition with continuous changes of temperature, especially in the cooling process. With the combination of the different polarized lights, we employ optical SHG as a nonlinear optical interfacial probe to study the liquid(solid)/vapour interface of the Ga-Bi liquid binary alloy. A surface phase transition from liquid-state to solid-state is observed when the temperature is decreased just below the monotectic temperature (222°C). In addition, it is interesting to find that there exists a difference between surfacial and bulky solidification (melting) behaviours.

2.Experiment

The SHG experimental set-up can be referred to Refs.[7]–[11]. A Q-switched 1064 nm Nd-YAG laser (Lumonics, Rugby) is used as a high-intensity light source for SHG(pulse duration 4 ns, pulse energy 12 mJ per pulse and repetition rate 5 Hz). A part of the incident light is separated from a splitter into a KH_2PO_4 (KDP) crystal, which also generates a signal with frequency 2ω. This serves as a reference against which the collected SH signals are normalized to eliminate the effects of fluctuation in the incident laser intensity. The SH signals detected by the photomultiplier tube (PMT) and the reference signals from the KDP crystal are sampled by a digital oscilloscope (LeCroy, Chestnut Ridge) and stored in a personal computer which integrates over the duration of the sampled pulses. The incident laser beam, with a spot size of approximately 1.5 mm in diameter, is polarized parallel (p) or normal(s) to the plane of incidence, depending on the position of the half-wave plate. High- quality Glan–Taylor polarizers are used for identifying p- or s-input light and detecting the p- or s- SH-output. The combination of input and output polarizations: $I_{2\omega}^{pp}$, $I_{2\omega}^{sp}$, $I_{2\omega}^{ss}$, $I_{2\omega}^{ps}$ (=p-in, s-out), is of some importance as described below. Generally, the p-component of the detected SH-signal gives the isotropic components of the surface second-order polarization susceptibility χ^s tensor, whereas the s-polarized SH-output mainly measures the anisotropic components of the nonlinear susceptibility tensor.[24] We assume that the normalized integral, $I_{2\omega}/I_{\mathrm{Ref}}$, is proportional to the number of SH photographs generated at the liquid(solid)/vapour interface of the Ga-Bi system.

Ga-Bi samples were prepared from the high-pure ingot metal Ga(99.9999%, Alfa/Johnson-Matthey, Germany) and ingot metal Bi(99.999%, ABCR GmbH, Germany). Special attention was given to the preparation of a high-pure liquid metallic sample and a highly clean surface in order to reduce the influence of oxygen impurities on the interface phase transition. The Bi and Ga materials were molten from a syringe and dropped into a Mo-crucible in a UHV quartz tube. The syringe was used so that impurities can be stuck on the wall of it. The crucible with the sample in vacuum was transferred into a big UHV chamber. The total pressure was typically 9×10^{-7} Pa when the chamber was cooled down to room temperature. An Ar^+ sputtering gun (Microtech' Model IG5, Oxford Applied Research) was used to in situ clean frequently the liquid surface during the measurements. SH-signals could be continuously recorded with the change of the crucible temperature. A heating or cooling rate of 7.2°C/h was adopted to slowly change the temperature of the sample so as to reach phase equilibrium. Normally, it took one week to increase the temperature from room temperature to 280°C, and another week to decrease the temperature down to room temperature. At the highest temperature point,

the temperature was held for 24 h. The error of the temperature measured was about ±2°C. Of course, a difference of temperature existed between the bulk phase and the interface. It was found[8−10] that the temperature at the surface was only a few degree of Kelvin below the bulk temperature. With increasing temperature, the composition of the liquid Ga-rich phase would change along the curve of solid/liquid and liquid/liquid coexistence, which is given in the Ga-Bi phase diagram,[25] as shown in Fig.1.

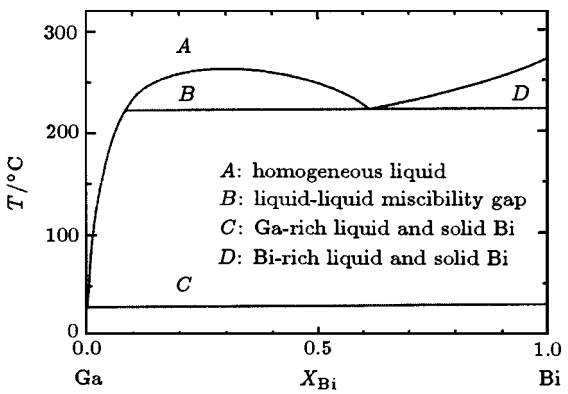


Fig.1. Phase diagram of the bulk Ga- Bi binary alloy.

3. Results and discussion

Firstly, in order to study the liquid/vapour interface of the Ga-Bi system, we prepare a pure Bi sample. Figure 2 shows the variations of SH-intensities ($I_{2\omega}^{pp}$, $I_{2\omega}^{ss}$) with decreasing temperature. With the melting point at 271°C, the SH-intensities between 290°C and 271°C come from the liquid/vapour interface and those between 271°C and 243°C come from the solid/vapour interface. It can be seen that $I_{2\omega}^{ss}$ from the solid surface is very different from that from the liquid surface: $I_{2\omega}^{ss}$ from the liquid surface is very small ($I_{2\omega}^{pp} \gg I_{2\omega}^{ss}$) and that from the solid surface is very large ($I_{2\omega}^{ss} > I_{2\omega}^{pp}$), while $I_{2\omega}^{pp}$ has a great change from smooth to fluctuated. Obviously, the change of SH-intensities at the melting point of pure Bi is only due to the interfacial phase transition from liquid-state to solid-state. The p-polarized component of the incoming and detected light generally measures the isotropic components of the χ^s tensor. So a strong $I_{2\omega}^{pp}$ from the Coulomb liquid surface is expected. The s-polarized SH-intensities mainly come from anisotropic components of the nonlinear susceptibility tensor. Thus, the $I_{2\omega}^{ss}$ from the isotropic Coulomb liquid surface should be near zero. This is consistent with our experimental results. Also, this implies that there exists the contribution of anisotropy from the solidified metallic surface. We can also see that the SH-intensities from solid surface are strongly fluctuated, since the solid surface continually changes with decreasing temperature and is not optically flat. On the other hand, a bulk undercooling phenomenon is observed from 271°C down to 262°C. In the undercooling process, the SH-intensities still come from liquid surface and are the same as that from the normal liquid surface (see process 1 in Fig.2). After reaching the undercooling end point of 262°C, the temperature suddenly jumps up to 271°C (see process 2 in Fig.2), maintaining for about 14 min, until the liquid phase begins to solidify. As a result, the SH-intensity $I_{2\omega}^{ss}$ suddenly becomes very large when the temperature is just below the point at 271°C, and $I_{2\omega}^{pp}$ first decreases and then increases again (see process 3 in Fig.2). On the other hand, this means that SHG is also suitable for detecting a surface phase transition from a liquid state to a solid state, at least, in a metallic system with the combination of different polarizations.

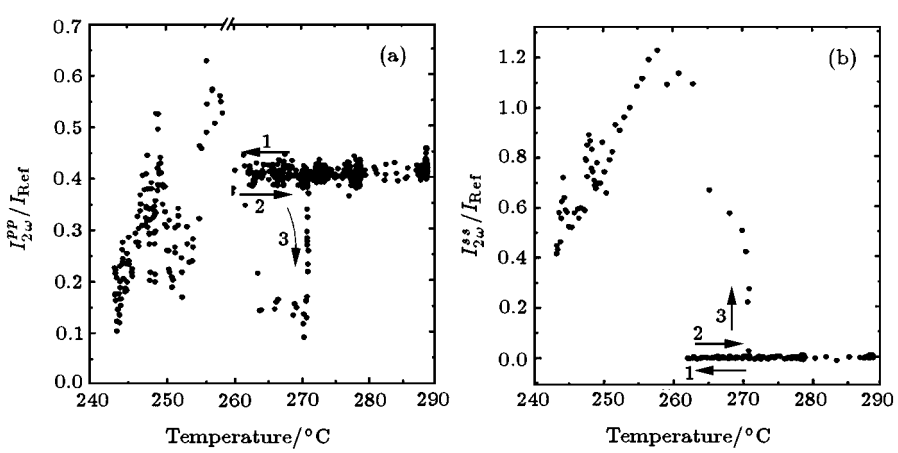


Fig.2. Variations of SH-intensities ($I_{2\omega}^{pp}$, $I_{2\omega}^{ss}$)from liquid(solid)/vapour interface of the pure Bi sample with decreasing temperature.

Why is the $I_{2\omega}^{ss}$ from the solidified surface so large? We have tried to measure an optically flat Cu or Al film surface using SHG. It is found that only $I_{2\omega}^{pp}$ is very large. So the solidified metallic surface from a liquid-state is very different from an optically flat metallic surface. We guess that the solidified metallic surface is similar to a stepped metallic surface,[26−28] which can cause very large changes of $I_{2\omega}^{sp,ps,ss}$ values.

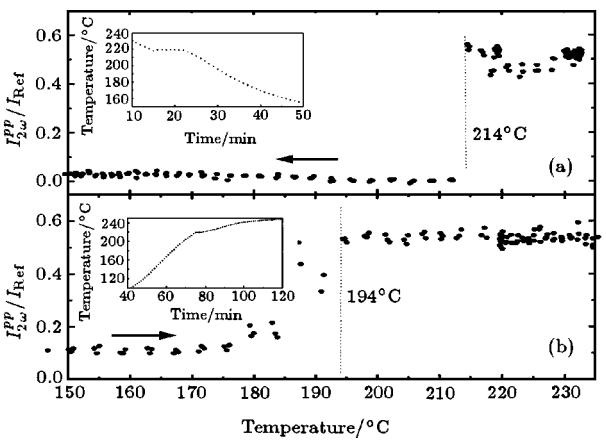


Fig.3. Variations of SH-intensities $I_{2\omega}^{pp}$ from liquid(solid)/vapour interface of the $Ga_{0.64}Bi_{0.36}$ sample in the cooling (a) and reheating (b) processes between 240°C and 150°C.

Furthermore, the samples are prepared with compositions of $Ga_{0.64}Bi_{0.36}$ and $Ga_{0.74}Bi_{0.26}$, which lie at the right- and left- hand sides of the critical point(262°C), respectively, as shown in Fig.1. In the first heating process from 35°C to 300°C, we cannot observe any apparent change or detect the expected surface phase transition, such as the wetting phenomena, by SHG. Possibly the optical SHG may be difficult to distinguish between the signals from the Bi-rich liquid phase and those from the Ga-rich liquid phase, if the transition really exists. However, the variations of SH-intensities from the liquid/vapour to solid/vapour interface of the $Ga_{0.64}Bi_{0.36}$ sample with decreasing temperature from 235°C to 150°C are very interesting. From Fig.3(a), $I_{2\omega}^{pp}$ is very large in the range from 235°C to 214°C. The surface appears to be a liquid-state seen with naked eye. Furthermore, an abnormal change of the SH-intensities $I_{2\omega}^{pp}$ happens at 214°C: $I_{2\omega}^{pp}$ decreases sharply and is nearly zero from 214°C to 150°C, as shown in Fig.3(a). This is nothing but the interfacial phase transition from a liquid-state surface to a solid-state surface in the cooling process. From the bulk Ga-Bi phase diagram, the Ga-Bi monotectic point is 222°C and the melting point of pure Ga is 29.9°C. Thus the solid film formed on the surface at about 214°C is neither gallium nor the oxides of Ga and Bi. The only possibility is that a Bi-rich phase is solidified atop the Ga-rich phase. This is different from the knowledge of Bi-Ga bulk phase diagram: above the critical point at 262°C, the thermodynamic stable phases are only vapour and one homogeneous liquid phase. The homogeneous liquid phase is then separated into two demixing liquid phases at temperatures between 262°C and 222°C: Bi-rich and Ga-rich liquid phases. Normally, the Bi-rich liquid phase should lie at the bottom and Ga-rich liquid phase should be atop because of the difference of density. Between 222°C and 30°C, the bulk Bi-rich phase should be solidified at the bottom and the liquid Ga-rich phase should be still above it. In any case, the surface should be liquid-state above 30°C. However, the reality is beyond our expectations. This abnormal experimental result has been also reported in Refs.[11] and [12].

Especially, the surface solidification and bulk solidification of the Bi-rich phase are different from each other. We know that the measured temperature corresponds to the bulk sample temperature, and SH-signal gives us the information of the sample surface. From the inset of Fig.3(a), the bulk Bi-rich phase is solidified at 220°C, with a slight undercooling about 2°C. Whereas the Bi-rich film is solidified at 214°C. Moreover, a macroscopically thick solid film floating on the liquid surface can be seen with naked eye when the crucible is shaken slightly. Sometimes, the solid film is not optically flat, the reflected light beams are out of the detected direction of the PMT, and thus the detected SH-intensities become nearly zero. When a measurement cycle is over, the sample is taken out of the UHV chamber at room temperature, the sample is heated up just above the melting point of pure Ga at 29.9°C, a solid film is really found to float on the Ga liquid phase and can be mechanically dislodged. The composition of the solid film is roughly analysed by TEM, it composes mainly of Bi. From the colour, we can also determine that it is Bi, because the colour of solid Bi is different from that of solid Ga.

After laying overnight at room temperature, if the sample with the solid surface is heated again, the solid surface will melt at a relative lower temperature than 214°C. Figure 3(b) shows the variations of SH-intensities with increasing temperature from 150°C to 235°C. The SH-signals $I_{2\omega}^{pp}$ from 150°C to about 180°C result from the solid surface. The solid film begins to

melt between 180°C and 194°C and the SH-signals above 194°C come from the liquid surface. On the other hand, the bulk Bi-rich phase is melted at about 222°C, as shown in the inset of Fig.3(b). We can see that the surface melting point is lower by about 20°C than the surface solidifying point. This implies that the phase of the Bi-rich solid film is a long-lived metastable phase. Similar phenomena were also observed and discussed by Rutledge and Taborek,[29] Bonn *et al*[24] in helium and caesium, cyclohexane and methanol systems. They thought that a first -order transition was always accompanied by hysteresis, i.e. resulting in a metastable phase.

Sometimes, the bulk and surface solidification behaviours are very different from each other, mostly depending on the purity of the sample and its surface condition. In the meantime, the temperature gradient may also play an important role. A temperature gradient applied to a liquid mixture not only causes a heat flux but also gives rise to a diffusion current of the constituent components (phases). The resulting separation of the phases causes a concentration gradient parallel or antiparallel with respect to the temperature gradient. The cross effect between temperature and concentration is known as thermal diffusion or Ludwig–Soret effect.[30] As for our samples, there is temperature difference of a few Kelvin from the surface to the bottom, which may induce a concentration gradient. However, we cannot determine whether the observed surface phase transition is due to the Ludwig–Soret effect or due to the wetting transition which is caused by the difference of surface tension of two phases. Also we try to hold the temperature constant for one day or more; however, the surface does not change at all. The surface transition appears only at a certain point in the cooling process. Here we give another example. Figure 4 illustrates the bulk undercooling curve and the variation of $I_{2\omega}^{pp}$ from the liquid(solid)/vapour interface of the $Ga_{0.74}Bi_{0.26}$ sample with decreasing temperature. In the cooling process, the temperature is first undercooled down to 214°C, and then jump back to the monotectic point 222±2°C, as shown in Fig.4(a). In the meantime, the SH signals form an apparent small cycle between 214°C and 222°C, as shown in the dotted square frame in Fig.4(b). And then, the SH-intensities $I_{2\omega}^{pp}$ still remain constant until the temperature decreased to 200°C, as shown in Fig.4(b). This implies that the sample surface remains in a liquid state from 222°C to 200°C and begins to solidify below 200°C in spite of the solidification of the bulk Bi-rich phase at 222°C, through undercooling to 214°C. After all, there is temperature difference of 20°C between the bulk and surface solidification. Can the Soret-effect caused by a temperature difference of a few degree of Kelvin induce such a big difference? It is possible that both surface tension and temperature gradient together induce the surface phase transition.

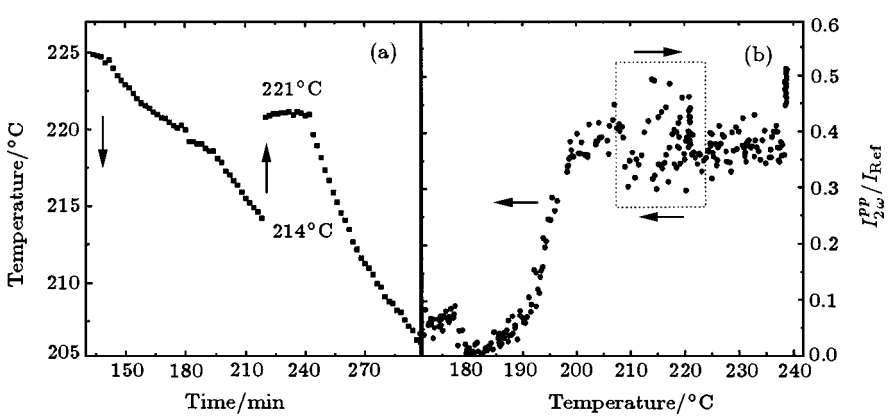


Fig.4. The bulk undercooling curve and the variation of $I_{2\omega}^{pp}$ from the liquid(solid)/vapour interface of the $Ga_{0.74}Bi_{0.26}$ sample with decreasing temperature.

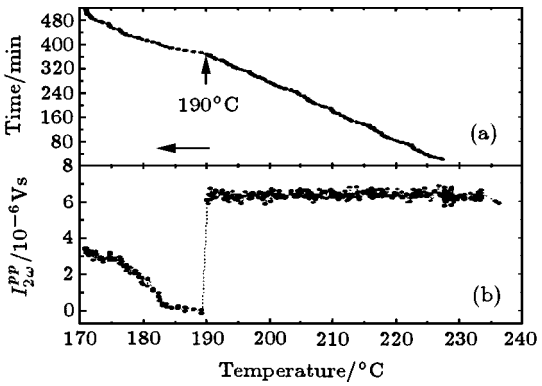


Fig.5. The cooling curve (a) and the variation of $I_{2\omega}^{pp}$ (b) from the liquid(solid)/vapour interface of the $Ga_{0.94}Bi_{0.06}$ sample with decreasing temperature.

A sample of $Ga_{0.94}Bi_{0.06}$ was also prepared, this composition lies at the solid-liquid coexistence line. The corresponding bulk phase transition from solid state to liquid state occurs at 190°C, as shown in Fig.1. It has not been reported that there exists any surface phase transition, including wetting phenomena, in the compositional ranges ($x < 0.08$ in $Ga_{1-x}Bi_x$) except in Ref.[12]. The wetting phenomena are considered to appear only in the compositional range where the miscibility gap exists. However, when the sample is cooled from 235°C to 170°C, the SH-signals have a significant change at 190°C, implying a surface phase transition. Obviously, this temperature corresponds exactly to the bulk phase transition from liquid state to solid state. Figure 5 gives the cooling curve (Fig.5(a)) and the variations of $I_{2\omega}^{pp}$ with decreasing temperature (Fig.5(b)), showing that $I_{2\omega}^{pp}$ keeps constant above 190°C and then drops down sharply to nearly zero at 190°C. Compared with other experimental results, this change means a surface phase transition from liquid state to solid state, which is concurrent with the bulk phase transition. This also means that the surface consists of not a Ga-rich phase but a Bi-rich phase. This fact is important since the solid Bi-rich film is also formed atop the surface in the $Ga_{1-x}Bi_x$ ($x < 0.08$) sample. The surface phase transition can be well reproduced in either heating or cooling process. However, no obvious undercooling and different surface solidification behaviours are observed in this sample.

4. Conclusion

In summary, SHG, as an effective nonlinear optical interfacial probe, is used to detect the surface behaviours in the liquid(solid)/vapour interface of the binary metallic systems. It has been observed that a macroscopically thick Bi-rich solid film floats on the Ga-rich liquid phase just below the monotectic temperature in the cooling process. In addition, there is an obvious difference between the bulk and surface undercooling behaviours, as well as between the bulk and surface solidification (melting) temperatures. This implies that we cannot absolutely describe a surface behaviour simply by the bulk phase diagram of an alloy. We have shown that SHG is suitable to detect a surface phase transition from liquid state to solid state in metallic systems.

Acknowledgments

This work was carried out in Professor Werner Freyland' laboratory at Karlsruhe University in Germany. So authors would like to thank Professor W. Freyland and Dr. D. Nattland for their great help.

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