

Structural investigations of the amorphous alloy $\text{Al}_{30}\text{Ge}_{70}$ under high pressure

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The structural behavior of the amorphous phase $\text{Al}_{30}\text{Ge}_{70}$, obtained by pressure quenching, has been investigated under pressure by *in situ* energy dispersive x-ray diffraction (EDXD) using synchrotron radiation. At $p \approx 5$ GPa there is a reversible transition from the amorphous state to a crystalline state with simple hexagonal (sh) structure. This γ phase is stable up to 47 GPa. At this pressure a transition to a hexagonal closed-packed structure takes place. The behavior of $\text{Al}_{30}\text{Ge}_{70}$ under pressure is discussed in connection with structural transformations of group-IV elements and III-V compounds.

I. INTRODUCTION

The binary system aluminum-germanium has a simple eutectic phase diagram with low mutual solubility of the components.¹ Recently, a new phase has been obtained for the alloy $\text{Al}_{30}\text{Ge}_{70}$ by high pressure action at elevated temperature and subsequent quenching to 77 K and release of the pressure.² X-ray-diffraction studies of the quenched alloy reveal a simple hexagonal (sh) structure (γ phase). On heating the metastable γ phase to room temperature amorphization takes place.²

In this work the effect of pressure on the amorphous alloy $\text{Al}_{30}\text{Ge}_{70}$ is studied by *in situ* energy dispersive x-ray diffraction (EDXD) experiments at ambient temperature in order to investigate the stability of the amorphous state under pressure and to get a better understanding of the nature of the amorphous alloy.

II. EXPERIMENT

Energy dispersive x-ray diffraction (EDXD) with synchrotron radiation at HASYLAB (DESY) has been used to study the behavior of the amorphous alloy under high pressure. The experimental setup with diamond anvil cell (DAC) and ruby manometer has been described previously³ as well as the preparation of the amorphous alloy $\text{Al}_{30}\text{Ge}_{70}$ by pressure quenching.² At ambient conditions the amorphous state of the alloy is stable for years. Nevertheless, grinding of the sample to fine powder was performed only at low temperature to avoid any recrystallization. White mineral oil was used as pressure transmitting medium. The pressure was determined either from the fluorescence of ruby splinters⁴ or from the compression of gold powder⁵ inserted into the high-pressure cell.

III. RESULTS AND DISCUSSION

When pressure is applied to the amorphous sample of $\text{Al}_{30}\text{Ge}_{70}$ it readily transforms to a crystalline state as documented in Fig. 1. A number of runs shows that crystallization starts at 4.3 GPa with a completion of the transition at 5.5 GPa.

From the powder diffractogram Fig. 1(b) it is evident that the crystalline phase is the very same γ phase which was obtained by the quenching experiments.² The lattice parameters of this simple hexagonal structure extrapolated to zero pressure are $a_0 = 284 \pm (7)$ pm, $c_0 = 261 \pm (7)$ pm with $c/a = 0.920$ (Fig. 2) in good agreement with the values $a = 283$ pm and $c = 262$ pm determined for the quenched sample at 77 K.²

This γ phase appears in many electron-rich alloys with electron concentrations around four electrons/atom. Initially, this structure was observed at ambient conditions in various Sn-based alloys.¹ Later, it was also seen in some alloys produced by splat cooling⁶ or pressure quenching⁷ and for the pure elements Si (Refs. 8 and 9) and Ge (Ref. 10) as well as for some III-V compounds¹¹ and Si-Ge alloys.¹² In this work the sh phase is observed for the first time in a binary Al-Ge alloy *in situ* under pressure. It should be noticed that the γ phase occurs in this alloy already at around 5 GPa, whereas the original formation of this γ -phase alloy by barothermal treatment of the eutectic sample required pressures around 9 GPa and temperatures above 300°C. On the other hand, in pure Ge the sh phase appears only at much higher pressure around 75 GPa. This is in accordance with the stated rule⁷ that intermediate phases in binary systems appearing at low or ambient pressure are often isomorphic with high-pressure modifications of the constituent elements.

On releasing the pressure the γ phase transforms back around 3 GPa to the amorphous state as shown in Fig. 1(d),

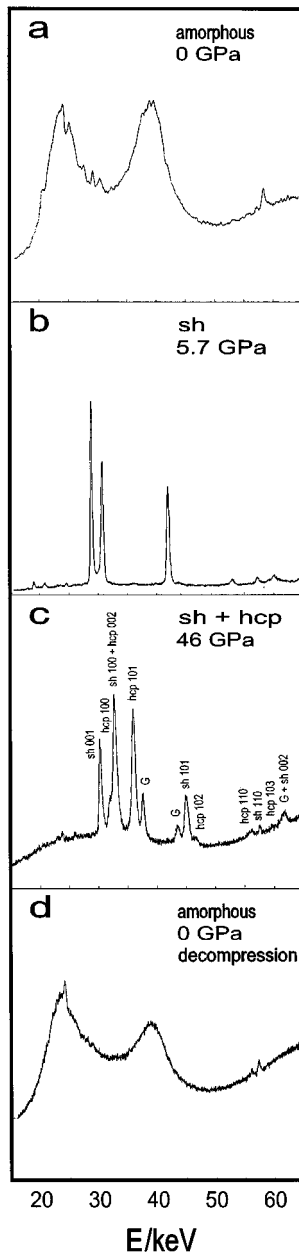


FIG. 1. Energy dispersive x-ray-diffraction (EDXD) spectra of the alloy $\text{Al}_{30}\text{Ge}_{70}$ under pressure. (a) gives the initial state of the amorphous alloy, (d) after pressure release. Additional diffraction lines from the gasket material are marked by G .

i.e., the transition amorphous-crystalline is reversible. The transitions back and forth are very rapid; within the few minutes needed to change the pressure and start the measurement, the transition is complete. So, even at room temperature the γ phase does not decompose to the equilibrium state $\text{Al}(\text{Ge})+\text{Ge}$ on pressure release but forms a metastable homogeneous amorphous state. The diffraction pattern of this amorphous phase was shown to have the characteristic features of the amorphous semiconducting state of pure Ge.¹³ The reversibility of the amorphous-crystalline transition with increasing and decreasing pressure shows the relative stability of this amorphous state. The high diffusion hindrance prevents the alloy from decomposition into the more stable two-phase state at normal pressure.

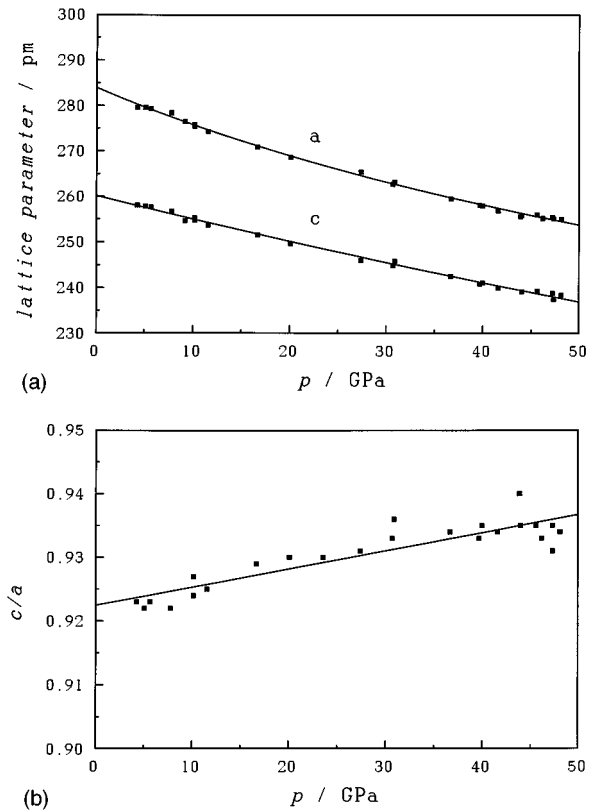


FIG. 2. Lattice parameters and aspect ratio c/a for the γ phase of $\text{Al}_{30}\text{Ge}_{70}$ under pressure.

The γ phase of $\text{Al}_{30}\text{Ge}_{70}$ is stable up to 49 GPa. With increasing pressure the c/a ratio increases slightly from 0.922 at 4 GPa to 0.935 at 49 GPa as shown in Fig. 2. Similarly, a slight increase in c/a from 0.937 to 0.947 in the pressure range from 16 to 34 GPa has been observed for sh Si.^{8,10} Also most of the alloys stabilized in the sh structure show similar values for c/a due to a special balance of real and reciprocal lattice contributions in the Ewald sum for the sh lattice, when $c/a \approx c^*/a^* = (\sqrt{3}/2)^{1/2} = 0.93$.¹⁴

With any of the common equations of states¹⁵ one obtains for the free parameters the values $V_0 = 0.01825(6) \text{ nm}^3$, $K_0 = 110(5) \text{ GPa}$, $K'_0 = 2.1(5)$, where V_0 is the average

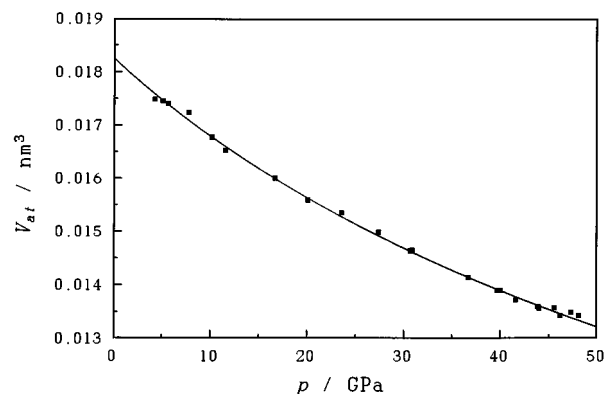


FIG. 3. Average atomic volume V_{at} of $\text{Al}_{30}\text{Ge}_{70}$ under pressure. Solid line represents the equation of state for the γ phase with the fitted parameters $V_0 = 0.01825(6) \text{ nm}^3$, $K_0 = 110(5) \text{ GPa}$, $K'_0 = 2.1(5)$.

atomic volume and the given uncertainties represent only the (statistical) standard deviation. (See Fig. 3.) The small value of $K'_0 = 2.1$ indicates thereby some "reduced stiffening"¹⁵ and such behavior has been observed before for the heavier elements of group Ia, IIa, and IIIb, where the *s-d* electron transfer accounts for these anomalies.¹⁶ Thus, also for the present alloy the EOS data give a hint for changes in the electronic structure under pressure.

At about 47 GPa a new phase appears as illustrated in Fig. 1(c), but the transition is still not complete at 49 GPa, the highest pressure achieved in these experiments. The analysis of the high-pressure EDX powder diffractogram reveals a hexagonal closed-packed (hcp) structure for the new phase with lattice parameters $a = 261.7$ pm, $c = 439.4$ pm, at 47 GPa. The decrease in volume at the transition from the sh to the hcp phase is about 2.5%.

It is interesting to note that the behavior of the alloy $\text{Al}_{30}\text{Ge}_{70}$ is similar to the behavior of Si, Ge and their alloys under high pressure. In all these cases there is a sh phase

which transforms ultimately to the closed-packed hcp structure; only for Si there is a narrow intermediate phase, Si(VI). For hcp $\text{Al}_{30}\text{Ge}_{70}$ the aspect ratio $c/a = 1.679$ is larger than the "ideal" value 1.633 but similar to hcp Si(VII) (1.70).^{8,9}

In conclusion, at 5 GPa and room temperature there is a *reversible* transition from the amorphous state of $\text{Al}_{30}\text{Ge}_{70}$ to a crystalline state. In the crystalline state the behavior of the alloy $\text{Al}_{30}\text{Ge}_{70}$ is similar to the behavior of the pure elements Si and Ge and their alloys under pressure but the range of stability for the sh phase of $\text{Al}_{30}\text{Ge}_{70}$ is much increased in comparison to the Si-Ge alloys.

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