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The Crystal Structure of a Metastable Binary Phase Related to β-Ga: β′-Ga(In)

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A metastable Ga–In phase with 9–12 at.% In has been prepared by rapid quenching (splat cooling) to ~80°K. The structure of this phase was found to be orthorhombic, α-U type, *Cmcm*, $a_0 = 2.770 \pm 1$ Å, $b_0 = 8.183 \pm 4$ Å, $c_0 = 3.306 \pm 2$ Å, V/atom $= 18.73 \pm 2$ Å^3 (at 10 at.% In and ~80°K), with disordered $Ga_{1-x}In_x$ atoms in position 4(*c*) with $y = 0.127 \pm 4$. β′-Ga(In) is structurally closely related to monoclinic β-Ga, and it can be considered as a distorted metastable binary extension of β-Ga.

Introduction

Ga does not form equilibrium intermediate phases with its four immediate vertical and horizontal neighbors in the periodic table, i.e., Al and In in the same group and Zn and Ge in the same period (*1*). However, it has been observed (*2*) that metastable Ga-rich phases can be retained by rapid quenching from the melt (splat cooling) in the systems Ga–Al (*3*), Ga–In (*2*), and Ga–Zn (*4*); these phases have been listed in a comprehensive review (*2*) as ψ phases (*5–7*). The interest in their previously unreported structures is increased by the rich crystal chemistry of elemental Ga. Ga has at least three structurally identified metastable modifications, β (*8*), γ (*9*), and δ (*10*), in addition to the equilibrium form α-Ga; these nonequilibrium phases had been prepared by supercooling Ga droplets to their respective metastable (constrained equilibrium) melting points (*11*).

The structure of the metastable Ga–In phase (*2*) has now been identified and is reported here; for reasons to be discussed below, it is designated as β′-Ga(In) in the following. The Ga–In system is simple eutectic (*1*); metastable equilibria in this system involving the metastable Ga modifications have been presented (*12*) and reviewed (*13*).

Experimental Methods and Results

Alloys of Ga with 9, 10, 11, and 12 at.% In were prepared from 99.999% pure starting materials. Metastable β′-Ga(In) was retained by rapidly quenching (splat cooling) small amounts of these alloys to about 80°K using the gun technique (*5*, *13*); X-ray diffractometer patterns of the quenched foils were taken at the same temperature with filtered Cu$K\alpha$ radiation. For details of the quenching experiments and the X-ray diffraction and calibration methods used, see

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Refs. (*3, 14, 15*). For each composition two alloys were quenched and investigated; both Cu and Pt substrates were used to eliminate interference of substrate diffraction peaks with those of β'-Ga(In). The powder diffraction patterns of β'-Ga(In) were single phase and contained 14 measurable lines in the range down to $d \sim 1.2$ Å and, in addition, 4 nonsystematic absences (see Table I) that could be used in the positional parameter refinement. The latter was carried out with a least-squares program (*16*) refining peak intensities rather than structure factors in order to utilize overlapping reflections. As shown in Table I, the patterns could be indexed in terms of an orthorhombic unit cell of the A20–α-U type (*17*) with $a_0 = 2.770 \pm 1$ Å, $b_0 = 8.183 \pm 4$ Å, $c_0 = 3.306 \pm 2$ Å, $\bar{V} = 18.73 \pm 0.016$ Å (at 10 at.% In), space group D_{2h}^{17}–*Cmcm*, and 4 atoms/cell in position

$$4(c): \pm(0, y, \tfrac{1}{4}; \tfrac{1}{2}, \tfrac{1}{2}+y, \tfrac{1}{4});$$
$$y = 0.127 \pm 4; \quad B = 1.3 \pm 0.9;$$

with standard deviations as given. The determination of the parameter y from the diffractometer intensities was complicated by preferred orientation effects; splat-cooled alloys often show substantial texture (*13*), which varies from one quenched foil to the next for the same composition. The condition for the absence of angular dependence of absorption in diffractometry (semi-infinite, flat sample shape and size) is also not well fulfilled for splat-cooled foils. The combination of these effects results in the relatively large R factor $R_I = \sum|I_0 - I_c|/\sum I_0 = 0.22$. The "intensity R factor" R_I is given here as the appropriate measure for an intensity refinement; however, it must be considered that R_I is larger than the commonly used R factor R_F based on F; thus for β'-Ga(In) one obtains $R_F = 0.17$. Further, the R values decrease substantially (to $R_F \sim 0.10$) if obviously texture-enhanced reflections such as (002) are eliminated and absorption corrections are made. The R values and the standard deviation of y are satisfactory in view of the inherently low quality of powder diffraction data for most rapidly quenched, metastable alloys (*13*). By comparison, $R_F = 0.08$ was obtained in a single-crystal study of metastable β-Ga (*8*).

Lattice parameters for this and the other β'-Ga(In) alloys are plotted in Fig. 1; it is seen that a_0 is almost constant while b_0 changes strongly with composition, accounting for most of the atomic volume expansion in the composition range between 9 and 12 at.% In.

The smallest interatomic distances for β'-Ga(In) with 10 at.% In are:

TABLE I

X-RAY DIFFRACTION PATTERN OF METASTABLE β'-Ga(In) WITH 10 at.% In AT ~80°K

	d (Å)		Intensity	
hkl	Obs[a]	Calc	Obs	Calc
020[b]	—	4.092	—	0.0
110	2.621(3)	2.624	41.3[c]	36.1
021	2.567(4)	2.571	58.7[c]	70.1
111	2.049(4)	2.055	69.7	35.1
040		2.046		16.7
130	1.944(5)	1.944	15.6	15.3
041	—	1.740	0.0	0.1
131	1.675(2)	1.675	13.2	15.0
002	1.653(6)	1.653	5.7	7.8
022	—	1.533	0.0	0.0
150	1.407(2)	1.409	5.6	3.5
112	1.399(2)	1.399	4.2	7.7
200	1.386(2)	1.385	10.6	3.8
060	—	1.364	0.0	0.0
220	—	1.312	0.0	0.0
151	1.295(3)	1.296	6.8	6.5
042	1.285(3)	1.286	5.3	5.5
061	1.260(2)	1.261	8.3	5.1
132		1.259		5.4
221	1.219(2)	1.219	10.7	8.8
240	1.148(1)	1.147	6.5	3.4

[a] Estimated reading and calibration errors in parentheses.

[b] Reflection outside the measured 2θ range.

[c] Intensities normalized to $I(110) + I(021) = 100.0$.

two first-nearest neighbors (in zigzag chains along c) with $r_1 = 2.66$ Å.

two second-nearest neighbors (along a) with $r_2 = 2.77$ Å, and

four third-nearest neighbors with $r_3 = 2.95$ Å.

Other interatomic distances are substantially larger; β'-Ga(In) is thus found to be 8-coordinated.

Discussion

The new phase is closely related to metastable β-Ga which has a monoclinic structure (space group $C2/c$) with $a = 2.766$ Å, $b = 8.053$ Å, $c = 3.332$ Å, $\beta = 92°02'$ at 248°K and Ga atoms in 4(e) with $y = 0.131$ (*8*); the structures of the two phases are almost identical except for the small monoclinic distortion which splits the fourfold set of the third-nearest neighbors in β'-Ga(In) into two twofold sets in β-Ga. β'-Ga(In) is thus a metastable, distorted (or, more properly, "un-distorted") binary extension of β-Ga; this is expressed in the designation, where the prime indicates the close relationship but nonidentity of the two structures. The β-Ga structure has been described as consisting of zigzag chains of atoms running in the c direction (*7*, *8*); however, the relatively small spread of the eight shortest distances, especially the first- and second-nearest neighbor distances, in β'-Ga(In) (as well as in β-Ga (*8*)) calls this interpretation of the structure of β'-Ga in question.

Figure 1 also shows the extrapolation of the cell parameters of β-Ga(In) to pure Ga and presents the corresponding values for

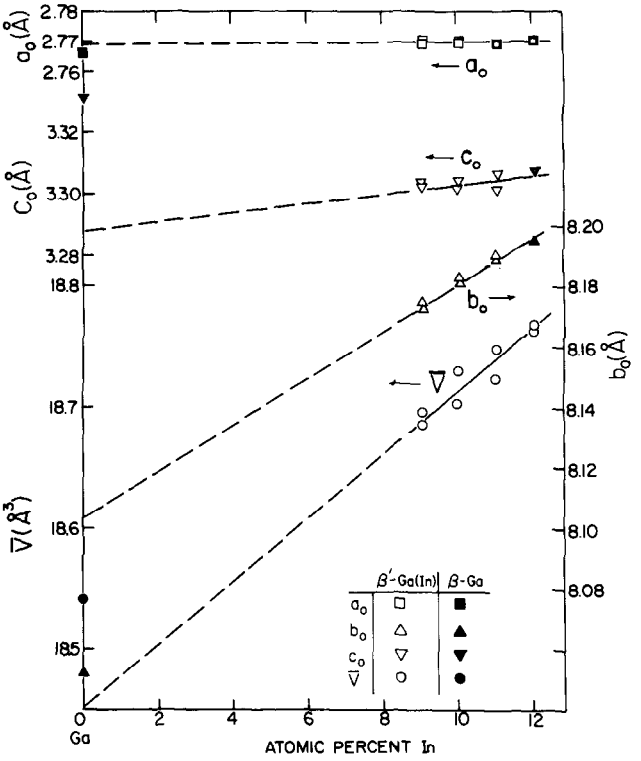

FIG. 1. Lattice parameters and mean atomic volumes $\bar{V}$ of metastable β'-Ga(In) alloys at ~80°K, with values for β-Ga (at 248°K (*8*)) shown for comparison.

β-Ga. The latter were taken at 248°K (*8*); their coefficients of expansion are not known but are probably highly anisotropic as are those of α-Ga (*18*). If the volume cofficient of expansion for α-Ga, $\alpha_V = 38.5 \times 10^{-6} {}^{\circ}K^{-1}$ (Ref. (*18*)) is used for β-Ga, a mean atomic volume at 80°K, $\bar{V}(\beta\text{-Ga}) = 18.42$ Å^3 is obtained; this agrees very well with the value $\bar{V}(\beta'_{\text{extrap}}) = 18.45 \pm 5$ Å^3 found by extrapolation to pure Ga (Fig. 1). As to the individual lattice parameters, $a_0(\beta\text{-Ga}) \sim a_0(\beta'_{\text{extrap}})$, $b_0(\beta\text{-Ga}) < b_0(\beta'_{\text{extrap}})$ and $c_0(\beta\text{-Ga}) > c_0(\beta'_{\text{extrap}})$; here, as for $\bar{V}$, the values for β-Ga and β'-Ga(In) are taken at 248 and 80°K, respectively. This suggests that $b_0(\beta\text{-Ga})$ and $b_0(\beta'\text{-Ga(In)})$ may have negative coefficients of expansion, as observed, e.g., for α-U (*19*) which is isostructural with β'-Ga(In).

Although in nonequilibrium experiments such as those presented here kinetic factors rather than thermodynamic ones may be controlling, some thermodynamic features of metastable Ga–In phases are suggested by experimental results on alloys with compositions outside the β'-Ga(In) forming range from 9 to 12 at.% In, as discussed in the following. Metastable Ga–In solid solutions with less than ~9 at.% In have the α-Ga structure (although with considerable changes of the lattice parameters and their ratios from those of α-Ga); the formation of β'-Ga(In) by rapid quenching of alloys with >9 at.% In may indicate that β'-Ga(In) becomes lower in free energy than metastable α-Ga(In) at this composition. At compositions above ~12 at.% In, multiphase mixtures with varying proportions of α-Ga(In), β'-Ga(In), and In were found after quenching, indicating that single-phase alloys β'-Ga(In) (or any other phase) with >12 at.%In are too high in energy to form from the melt or to be retained in this composition range regardless of their structure.

The possibility of a constrained equilibrium (*20*) between the two related metastable phases, monoclinic β-Ga and orthorhombic β'-Ga(In), is of special interest. Their structural similarity suggests the possibility of a gradual change of the angle β from 92.02° for β-Ga to 90° for β'-Ga(In), accompanied by a second-order phase transition between these phases. The temperature $T_{\beta-\beta'}$ of this transition is likely to change with composition. The composition where $T_{\beta-\beta'}$ is equal to the actual solidification temperature probably lies at < 9 at.% In and thus falls into the composition range where metastable α-Ga(In) is retained upon quenching; the β–β' transition is therefore unobservable with the present techniques. Use of a temperature-controlled X-ray diffractometer cold stage to measure the angle β as a function of temperature for both β-Ga and β'-Ga(In) could clarify this point.

The appearance of the metastable β'-type alloys is not unique to the Ga–In system; metastable phases with this or closely related structures were also found in quenched alloys of Ga with additions of Zn and Al (*3, 4*); however, their diffraction patterns have not yet been completely interpreted (*21*).

Crystal chemically, the appearance of the α-U type (or the distorted, derivative β-Ga type) in metastable *B*-metals and *B*-metal alloys is interesting; other than in β-Ga and one or more Ga-based phases, this type has also recently been found in a metastable Hg–In phase (*21*). The atomic coordination of β-Ga is related to that of a strongly rhombohedrally distorted fcc Cu-type structure such as that of α-Hg (*22*); the Cu type and its distortion variants are frequently favored in this periodic table region of *B*-element metals (*2*). Like α-Ga, the β-Ga and β'-Ga(In) types have substantial structural weights (intensities) lying at low momentum (reciprocal lattice) values (see Table I), contributing to their structural stability (*23, 24*); in addition, β-Ga has markedly lower atomic volume than α-Ga.

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