Reply to ''Comment on 'Phase equilibria of the Ga–Ni–As ternary system' '' [J. Appl. Phys. 82, 493 (1997)]

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We reply to the comment by Guerin and Guvarc'h concerning the phase equilibria of the Ga–Ni–As ternary system. We refute their position that the quench rate of the phase diagram samples is not important and that the solid-state phase equilibria of the Ga–Ni–As system does not change significantly between the temperatures of 25 and 800 °C. It is also demonstrated that the occurrence of ordered superlattice structures is not inconsistent with our work. We conclude that an adequate number of samples were prepared in our study to justify the modifications proposed to the Ga–Ni–As isothermal section and it is an accurate representation of the phase equilibria at 600 °C. © *1997 American Institute of Physics.* [S0021-8979(97)02512-7]

First, we would like to address two mistakes in the ''comment'' that may cause a misrepresentation of our work. In Fig. 1 of the ''comment'' sample GNA-14 (Ingerly *et al.*[1]) is drawn in the middle of the NiAs single-phase region. This is not correct, while sample GNA-14 is located close to the NiAs phase boundary, Fig. 1 of this response clearly shows it is located in the NiAs–$Ni_{11}As_8$ two-phase region. Figure 1 is a reproduction of the Ni-rich region of the Ga–Ni–As Gibbs isotherm at 600 °C found in Ingerly *et al.*[1] The accurate location of the other phase diagram samples mentioned in the ''comment'' are also included for the reader's easy reference.

The second misrepresentation occurs over our position on the possible existence of a ternary phase near the γ'-$Ni_{13}Ga_9$ binary, denoted phase C by Guerin and Guvarc'h.[2] In our manuscript we stated that ''the present investigation does not conclusively answer the question of whether phase C found by Guerin and Guivarc'h[2] is a ternary phase or a ternary extension of γ'-$Ni_{13}Ga_9$, as was suggested by Zheng *et al.*[3]'' We then went on to elaborate on the published evidence for both possibilities, detailing the reasons for the uncertainty and suggested that further x-ray diffraction (XRD) investigation would be required to resolve this issue. Additionally, the ternary extension of γ'-$Ni_{13}Ga_9$ shown in our Gibbs isotherm is drawn with dashed lines to reflect this uncertainty. Thus the additional experimental evidence concerning phase C is not inconsistent with our position.

Most of the discussion in the ''comment'' revolves around Guerin and Guivarc'h's belief that the diagram proposed in Ref. 2 is an accurate representation of the Ga–Ni–As system phase equilibria at temperatures between 25 and 800 °C. It is therefore possible to address many of the specific issues raised in the ''comment,'' with a few general remarks about the diagram proposed by Guerin and Guivarc'h.

For the phase diagram determination Guerin and Guivarc'h prepared 40 samples; these samples were homogenized at 1000 °C and slowly cooled to 800 °C. The samples were then either quenched or slowly cooled to room temperature; the importance of this will be discussed below. It should also be noted that they did not conduct a metallographic or compositional examination for any of their samples, relying exclusively on XRD. This is in contrast to Ingerly *et al.* where all the phase diagram samples were quenched after being subjected to long-term isothermal annealing, and for analysis both XRD and electron probe microanalysis were employed.

We have to disagree with Guerin and Guivarc'h when they suggest that the solid-state phase equilibria of the Ga-Ni-As system does not change significantly between the temperatures of 25 and 800 °C. They offer no experimental proof of this claim and it is clearly inconsistent with the behavior of the binary systems. Ingerly *et al.* also furnishes additional information showing that Guerin and Guivarc'h's assumption is not valid. A sample with a nominal composition of Ni_3GaAs(GNA-11) demonstrates that the observed crystal structure can be dependent on the cooling rate. The quenched sample shows a single-phase $B8_{1.5}$-type crystal structure while the slowly cooled sample exhibited additional peaks consistent with a superlattice type structure. Additionally, a solid-state reaction occurring between 450 and 460 °C

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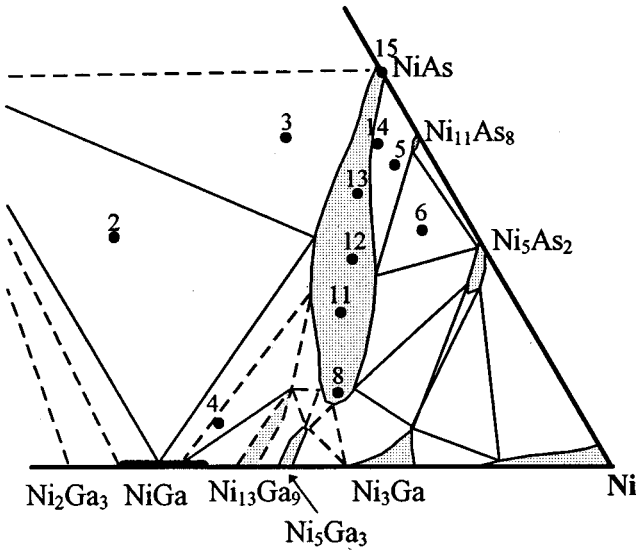

FIG. 1. The Ni-rich corner of the Ga-Ni-As Gibbs isothermal section at 600 °C as found in Ingerly *et al.* Black circles mark the atomic compositions of the samples.

was observed using DTA[1] and by Swenson[4] using DSC. These are very significant results when one considers that some samples prepared by Guerin and Guivarc'h were quenched while others were slowly cooled. When the methods used to prepare their phase diagram samples are examined in light of our findings it becomes obvious that the diagram proposed by Guerin and Guivarc'h cannot be regarded as an isothermal section.

We are not alone in these conclusions, in a review of the As-Ga-Ni phase diagram, Pratt[5] who is an authority on phase diagram and alloy thermodynamics gave the following comments concerning the work of Guerin and Guivarc'h:

> ''for reasons outlined earlier it cannot be regarded as an isothermal section; the thermal history of the alloys seems unlikely to have yielded equilibrium since no isothermal anneals were carried out in the solid state. The suggestion by Guerin and Guivarc'h[2] that the general features of this diagram may be taken to represent the form of the solid state phase diagram at all temperatures above 25 °C is not valid...''

We do not question the existence of the hexagonal superlattice phases found by Guerin and Guivarc'h.[2] We only assert that they are not thermodynamically stable at 600 °C. It is possible that the superlattice phases found by Guerin and Guivarc'h formed from the NiAs solution phase during slow cooling of their samples and are not stable at higher temperatures; the solid-state reaction observed between 450 and 460 °C supports this view. Because the diagram of Guerin and Guivarc'h cannot be considered an isothermal section it is not surprising that there are differences between the two works. The experimental evidence strongly supports that the Gibbs isothermal sectional proposed in Ingerly *et al.* accurately represents the phase equilibria in the Ga–Ni–As system at 600 °C.

To comprehensively address all the thin-film reaction studies cited in the ''comments'' would require more space than this reply is allotted. It is important to point out that due to a limited supply for one of the end phases in such a couple, the phases observed are time dependent. This phenomenon has been discussed in the literature.[6,7] Moreover, due to the relatively short annealing times it is possible nonequilibrium phases will form. Finally, the results of Guerin and Guivarc'h cite are for a wide range of reaction temperatures, so it is inappropriate to combine all the results on the 600 °C isothermal section. Therefore interpreting the thin-film reactions is not so straight forward as the ''comments'' might suggest and the studies do not prove or disprove either position.

In conclusion, the Ga–Ni–As isothermal section proposed in our work is an accurate representation of the phase equilibria at 600 °C. Our phase diagram samples where subjected to long term thermal annealing to insure they reached equilibrium and were of an adequate number to justify the modifications made. The diagram presented by Guerin and Guivarc'h does not represent an isothermal section. When this is considered with the additional experimental evidence given in our manuscript, particularly the effect of the cooling rate on the phase diagram samples, many of the comments are answered. We encourage everyone to read the original manuscript where we were able to discuss many of these issues in a more comprehensive manner.

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