Direct Evidence for Amorphization of Pure Gallium by Low-Temperature Ion Irradiation

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By combining low-temperature ($T < 10$ K) heavy-ion bombardment (275-keV Ar^+, 250-keV Ne^+) with an *in situ* low-temperature electron-diffraction technique, for the first time direct evidence could be provided that ion irradiation can result in a complete amorphization of gallium, i.e., of a pure metal without a second component stabilizing the amorphous phase. The results can be interpreted in terms of a spike model and are in close analogy to those found by vapor quenching onto a liquid-helium–cooled substrate.

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During the last years, ion implantation has proved to be a versatile technique to produce metallic amorphous systems[1,2] offering some specific advantages in comparison to more conventional quenching techniques. For instance, by implantation the composition of an alloy can be changed step by step within *one* sample giving the possibility of studying in detail the transition from the crystalline to the amorphous state. Two experimental procedures are usually applied. Either a chemically active species B is directly implanted into a crystalline target A or a sandwichlike structure consisting of alternating A-B layers is irradiated with chemically inert ions like Xe^+. In the first case, the radiation damage produced by the implantation of element B is also stabilized by this element, eventually leading to an amorphous alloy with a typical compositon of $A_{0.8}B_{0.2}$. Recent examples for this type of experiment are the implantation of phosphorous into nickel[3] or into niobium.[4] In the second case, in addition to the radiation damage, ion irradiation produces a rather uniform AB mixture by collisional mixing. An example for this type of experiment is the Xe^+ bombardment of crystalline Au-Si multilayered structures, which again leads to a homogeneous amorphous phase.[5]

The successful production of amorphous systems by implantation/irradiation led to a revival of the old idea[6] of spike phenomena.[7,8] In a spike model, the dynamical state during the lifetime of a collision cascade is considered as a collective motion of the involved atoms rather than a sequence of binary encounters, where a moving atom hits an atom at rest, as supposed by the linear cascade theory. Thus, it is very tempting to think of this state as a local liquid or even gas, depending on how the energy per atom within a cascade compares to the melting or sublimation energy of the target. This local state lasts only for a very short period, of the order of 10^{-12} s. This spike picture suggests, as an analogy to quenching experiments like vapor quenching onto liquid-helium–cooled substrates or splat-cooling of a melt, that we think of a cascade collapse as a local quenching event with an extremely high quenching rate of the order of 10^{14} K/s. If this simple spike picture holds, any system which can be made amorphous by, e.g., quench condensation onto a liquid-helium–cooled substrate is a candidate for an amorphization by implantation/irradiation. Thus, even a pure element like gallium (Ga) should become amorphous by only irradiating it, i.e., without implanting a stabilizing second component, since Ga forms an amorphous phase if quench condensed. Within the above picture, this conclusion hinges on the premise that the production of radiation damage is governed by spike phenomena. This, in turn, is much more likely for heavy projectiles than for very light ones, a point which will turn out to be crucial for a test of the spike model.

For such a test, Ga appears to be an ideal system for the following reasons. First of all, since it is a monocomponent system, there is no interfering chemical influence of a second species. In addition, three different phases can be distinguished[9]: The first is the amorphous phase (a-Ga) formed after vapor condensation onto a substrate at 4.2 K. Amorphous Ga exhibits a residual resistivity of $\rho_0 = 33$ $\mu\Omega$ cm and a transition temperature to superconductivity T_c of 8.5 K. This phase is stable only up to about 16 K, then it transforms into the metastable crystalline β phase (β-Ga) with a resistivity of 3 $\mu\Omega$ cm and a T_c value of 6.3 K. Eventually, at about 60 K, β-Ga transforms into the stable crystalline α phase (α-Ga) with a resistivity of 12 $\mu\Omega$ cm and a T_c of 1.07 K. From these data it is clear that the three Ga phases can be rather well distinquished by their resistivity and T_c values. But it is also clear that because of the low crystalliza-

tion temperature of a-Ga (16 K), any irradiation experiment which is supposed to result in the amorphous Ga phase has to be performed at low temperatures ($T < 10$ K). Such an irradiation experiment has been performed recently and revealed the following results[10]:

(a) Ar^+ irradiation (275 keV) of crystalline α-Ga results in an amorphous phase. The fluence necessary for a complete amorphization is 2×10^{14} cm^{-2}.

(b) Ar^+ irradiation of crystalline β-Ga under identical conditions does *not* produce the amorphous phase.

(c) He^+ irradiation (200 keV) of crystalline α-Ga does *not* result in the amorphous phase, even with He fluences corresponding to the same average number of displaced Ga atoms as for the Ar irradiation.

These statements were deduced from the observed behavior of the resistivity and the superconducting transition temperature. Since, to our knowledge, Ga is the only pure metal which could ever be transformed into a liquidlike amorphous phase by only irradiating it, a confirmation of the above results by a direct observation of the structural changes seems to be important. It is the aim of this Letter to provide such direct evidence by combining the low-temperature irradiation with an *in situ* low-temperature electron-diffraction technique.

To make possible a transmission electron diffraction measurement, the Ga films (typical thickness 30 nm) were prepared by evaporation onto a 10-nm carbon backing film spanned over a 20-μm Pt aperture. This sample holder was mounted in a ^{4}He-irradiation cryostat[11] and could be cooled down to 2 K. The crystalline α and β phases were produced by crystallization from the amorphous Ga phase prepared by vapor quenching onto the liquid-helium–cooled substrate. A 50-keV electron beam was used for the diffraction measurement, provided by an electron source with a far-focus lens system. Thus, no additional electron-optical devices were necessary. During the electron diffraction, the sample temperature always remained below 10 K. The diffraction patterns were registered by a photographic plate.

For the heavy-ion irradiations reported here, Ar^+ (275 keV) and Ne^+ ions (250 keV) were used. Again, during the irradiation the temperature of the Ga films stayed below 10 K. Further information on the low-temperature irradiation equipment can be found in Ref. 11. The experimental procedure will become clear by the following results.

Figure 1 shows the electron diffraction patterns of the three above-mentioned Ga phases. In Fig. 1(a) the as–quench-condensed amorphous phase can be seen, where only two broad rings can clearly be resolved. Figure 1(b) gives the pattern for the crystalline β phase, which is formed after heating the amorphous phase up to 16 K. After further heating of the β phase up to 60 K, the transformation into the stable crystalline α phase occurs, the diffraction pattern of which is shown in Fig. 1(c). This sample, exhibiting the α phase, is then cooled down to 4.2 K and irradiated with 275-keV Ar^+ ions. The corresponding fluence φ is 2×10^{14} cm^{-2}. The result of this irradiation is demonstrated in Fig. 2, where corresponding electron diffraction patterns are shown. Figure 2(a) gives the pattern of the α phase, i.e., the pattern of the sample *before* the Ar^+ irradiation. This is contrasted with the result *after* the Ar^+ irradiation, given in Fig. 2(b). Clearly, no crystalline rings are exhibited; only two broad rings can be resolved. This is typical of the amorphous phase as can be seen from a comparison to the pattern of the as–quench-condensed amorphous phase shown in Fig. 2(c). Thus, the conclusion drawn from the T_c and resistivity behavior, that Ar irradiation leads to a complete amorphization of the crystalline α-Ga phase, is directly confirmed. Annealing of this irradiation-induced amorphous phase results in the same phase transformation sequence (a-Ga

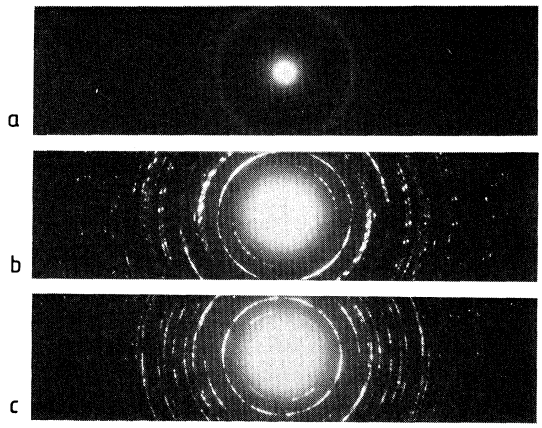

FIG. 1. Electron-diffraction patterns of different Ga phases. (a) Amorphous Ga produced by quench condensation onto a liquid-helium–cooled substrate, (b) β-Ga produced from the amorphous phase by heating up to 16 K, (c) α-Ga produced from the β phase by heating up to 60 K.

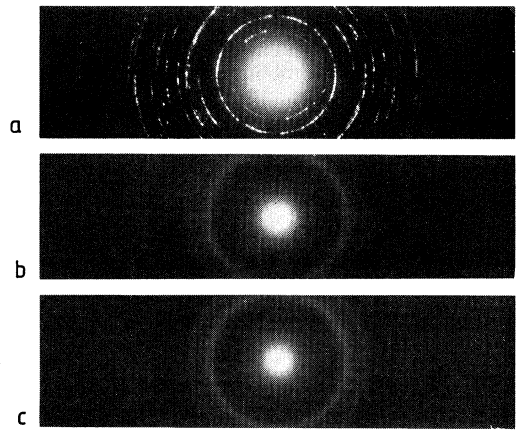

FIG. 2. Electron diffraction patterns of different Ga phases. (a) Crystalline α-Ga *before* Ar^+ irradiation, (b) amorphous Ga produced by irradiation of α-Ga with 275-keV Ar^+ at $T<10$ K (total Ar fluence $\varphi=2\times10^{14}$ cm^{-2}), (c) amorphous Ga produced by quench condensation.

$\rightarrow \beta$-Ga $\rightarrow \alpha$-Ga) as observed for the as-quench-condensed amorphous phase.

In a second experiment, the crystalline β phase was produced by heating up the as-quench-condensed amorphous phase. This β phase is then irradiated with Ar^+ ions under identical conditions as α-Ga, i.e., 275-keV Ar^+, $\varphi=2\times10^{14}$ cm^{-2}, $T<10$ K. The results are given in Fig. 3. Here Fig. 3(a) shows the diffraction pattern of the β phase *before* the Ar irradiation, and Fig. 3(b) shows the corresponding pattern *after* the Ar irradiation.

Clearly, β-Ga is stable against Ar irradiation; it cannot be transformed into the amorphous Ga phase. Again, this is a direct proof of what has been deduced from the T_c and resistivity behavior.

In Ref. 10 it has been demonstrated that He^+ irradiation (200 keV) of α-Ga, as opposed to the Ar^+ irradiation, does *not* result in the amorphous Ga phase, even with He fluences corresponding to the same average nuclear energy deposited per target atom Q as in the Ar case (Q divided by twice the displacement energy gives an estimate of the average number of displacements per target atom). This was interpreted as a strong support of the qualitative validity of the spike model. To get a better estimate of the upper bound of the projectile mass necessary to produce amorphous Ga, the α phase was bombarded with 250-keV Ne^+ ions. The resulting T_c changes are given in Fig. 4 as a function of Q together with the Ar and He results. Clearly, the Ne irradiation (closed

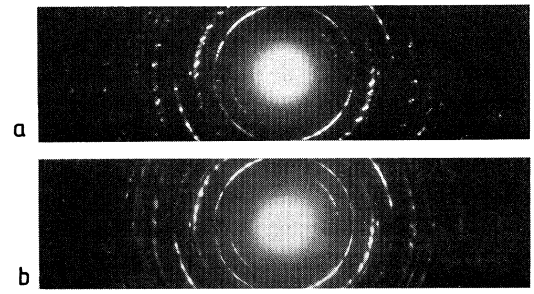

FIG. 3. Electron diffraction patterns of (a) crystalline β-Ga *before* Ar^+ irradiation and (b) *after* Ar^+ irradiation (275 keV, $T<10$ K, $\varphi=2\times10^{14}$ cm^{-2}).

circles in Fig. 4) also produces the amorphous Ga phase, as indicated by the resulting high T_c values. In addition, the Ne irradiation scales very well to the Ar irradiation when plotted as a function of Q. Figure 4 demonstrates the importance of the energy density within cascades for attaining the amorphous Ga phase by irradiation, i.e., the occurrence of spike phenomena seems to be crucial. On the other hand, under identical conditions, β-Ga cannot be transformed into the amorphous phase. This proves that, in addition to the occurrence of spikes, the crystalline phase surrounding a local amorphous phase plays an important role, e.g., by nucleating a recrystallization of the amorphous region. Such a recrystallization seems more likely the more similar the short-range orders (SRO) of the surrounding crystalline phase and the local amorphous phase. For Ga it is known from x-ray measurements[12] that the SRO of the melt is similar to the SRO of β-

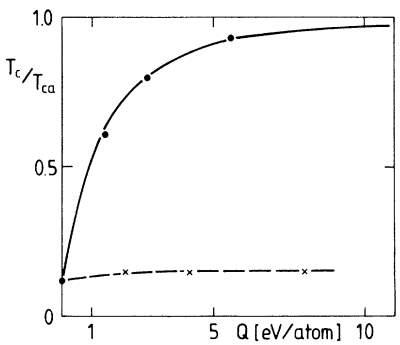

FIG. 4. Superconducting transition temperature T_c of α-Ga normalized to the value of the amorphous phase T_{ca}, as a function of the average nuclear energy deposited during irradiation with different projectiles. Solid line, 275-keV Ar^+; closed circles, 250-keV Ne^+; crosses, 200-keV He^+. Irradiation temperature is always below 10 K.

Ga, but quite different from that of α-Ga. Since, on the other hand, the amorphous Ga phase is "liquidlike," i.e., the SRO of a-Ga is very similar to the SRO of the melt, there follows a high similarity of the SRO of the amorphous phase and β-Ga, in contrast to α-Ga. We think that this similarity of the SRO in a- and β-Ga leads to a recrystallization of a locally amorphous phase produced by irradiation, thus preventing the irradiation-induced amorphization of β-Ga as opposed to α-Ga.

The different behavior of α- and β-Ga concerning the amorphization by irradiation has a close analogy in quenching experiments[13]: While the amorphous phase can be produced by quench condensation onto α-Ga as a substrate, it is *not* possible to form the amorphous phase by quenching onto β-Ga. Again, this can be interpreted as being due to the similarity of the SRO in the amorphous and the β phases.

In conclusion, the experiments have provided, for the first time, a direct proof of the possibility of amorphizing a pure metal by irradiation. The results are in close analogy to those of quench-condensation experiments and can be qualitatively interpreted in terms of a spike model.

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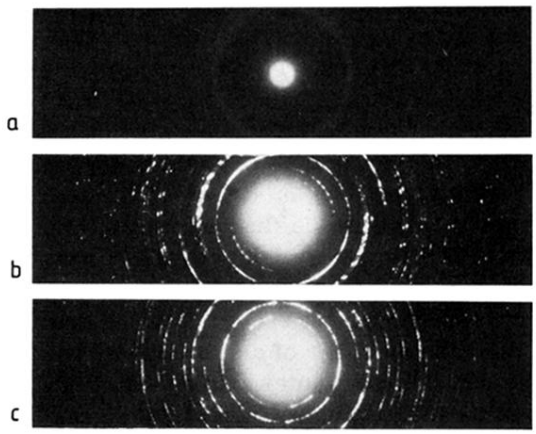

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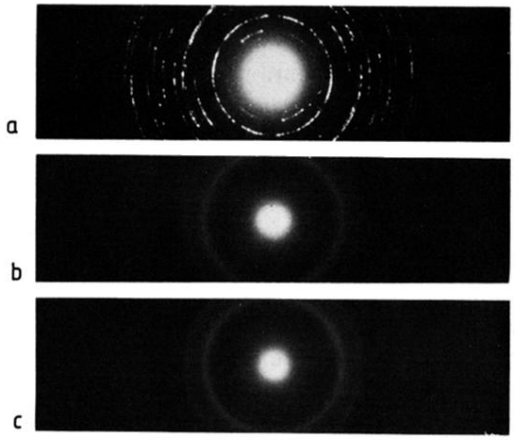

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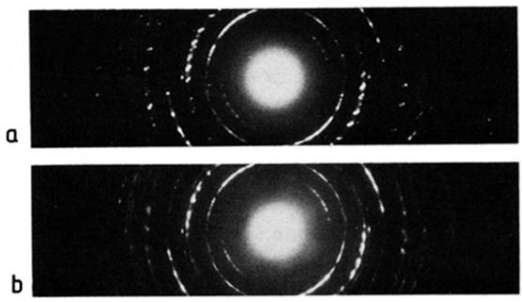

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