# Evidence for Amorphization of a Metallic Alloy by Ion Electronic Energy Loss

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Crystalline $Ni_3B$ ribbons have been irradiated at low temperature with GeV heavy ions (Kr,Xe,U) in order to study the disordering process induced in this material by ion electronic energy loss. The atomic rearrangements produced by irradiation were monitored *in situ* via electrical resistance measurements and characterized after annealing at room temperature by electron diffraction. The results show a huge electrical resistivity increase above an electronic-energy-loss threshold, which can be ascribed to partial amorphization of the irradiated alloy.

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It has been known for a long time that electronic excitation and ionization arising from the energy loss of energetic ions $[(dE/dx)_e]$ may induce structural changes in systems with a low electrical conductivity (e.g., formation of the so-called latent tracks in insulators).[1] Until recently, it was commonly admitted that no effect of this kind could exist in alloys containing a metallic character, due to the ability of free electrons to rapidly and efficiently smear out the perturbation caused by the ion beam. Lately, high-energy heavy-ion irradiation of a large variety of metallic alloys[2-8] has nevertheless proven that structural changes due to $(dE/dx)_e$ also occur in metallic systems *as long as they are in the amorphous state*. These studies demonstrated that electronic excitation leads, above a $(dE/dx)_e$ threshold, to (i) defect production with a cross section up to 2 orders of magnitude higher than that of elastic collisions, from the very beginning of the irradiation, and (ii) large anisotropic growth of the sample dimensions, above an incubation fluence depending on the material considered.

The question then arose of why the atomic rearrangements observed in an amorphous alloy could not occur in a *crystalline* one. A partial answer concerning the absence of the anisotropic growth phenomenon [observation (ii)] in irradiated crystalline metallic compounds[4] is given by a recent model[7] based on the assumption that the ion-beam-induced plastic deformation of amorphous materials would result from an ion-explosion-spike mechanism in a system where a collective motion of atoms is allowed by the absence of well-defined lattice sites. However, no experimental or theoretical arguments allowing the conclusion that defect production [observation (i)] could not take place in crystalline metallic targets have been put forward up to now. As a matter of fact, an enhancement of the damage rate due to electronic excitation has been recently observed in crystalline pure Fe (Ref. 9) and Ga.[10] These results suggest that far more dramatic disordering effects, such as amorphization of the irradiated target, might occur in a suitable system. The metal-metalloid compound $Ni_3B$ is a good candidate for such a study since it is known[11-13] to undergo a crystalline-to-amorphous transition above $\sim 0.1$ displacement per atom (DPA) by nuclear collisions. In a previous paper,[14] electrical resistance experiments performed on 3-GeV Xe-irradiated polycrystalline $Ni_3B$ ribbons revealed a very small (in the limit of the experimental uncertainties) effect of electronic energy loss for values of $(dE/dx)_e$ up to 3.7 keV/Å. A possible explanation of this negative result would be to consider that, as already demonstrated in amorphous alloys,

a material-dependent critical ionization density, i.e., a $(dE/dx)_e$ threshold, exists for the damaging process. A way to check this possibility was to perform the irradiation at a much higher $(dE/dx)_e$ value by using GeV ions of higher atomic number. Such an opportunity was offered by the availability of a GeV uranium-ion beam from the GSI accelerator in Darmstadt. The samples were irradiated at low temperature with high-energy heavy ions displaying a large range of $(dE/dx)_e$. An unambiguous effect of creation of disorder by electronic excitation in a crystalline metallic system is evidenced. At the highest value of the ion electronic stopping power studied, the observed disorder consists of amorphization.

Polycrystalline $Ni_3B$ ribbons ($\sim 20$ $\mu$m thick) were irradiated at low temperature (10 or 80 K) in the IRABAT facility with GeV heavy ions, either at GANIL-Caen (Kr and Xe) or at GSI-Darmstadt (U). Stacks of total thicknesses much smaller than the range of the irradiating ions allow us to vary the mean value of $(dE/dx)_e$ inside the samples from 1.2 to 7.2 keV/Å. Electrical resistance measurements were performed *in situ* during beam stops all along the irradiation using a standard four-probe technique. At the end of irradiation, the samples were heated up to room temperature, thinned down to $\sim 1000$ Å by successive ion milling and chemical etching, and analyzed by electron diffraction. Unirradiated samples prepared in the same way were also analyzed in order to check that the structural modifications observed after irradiation were not due to the sample preparation technique.

Figure 1 presents typical electrical resistance variations of the irradiated ribbons with the ion fluence for the various irradiations performed. The observation of the ribbons at the end of irradiation indicates that the huge deformation (due to the anisotropic growth) observed[14] in Xe-irradiated amorphous $Ni_3B$ has not occurred,[15] in agreement with previous results reported on crystalline metal-metal alloys.[4] The large value of $\Delta R/R_0$ obtained following U irradiation (more than 2 at a fluence of $4\times10^{12}$ ions cm$^{-2}$) can consequently be essentially ascribed to a resistivity increase due to creation of disorder by the ion beam. The demonstration that electronic energy loss is responsible for this irradiation-induced resistivity increase can be made by normalizing the slope of the resistivity data to the number $\Phi\tau$ of DPA created via elastic collisions by the incoming ions. Figure 2 presents the result of such a calculation versus the ion electronic stopping power. The large positive slope observed above a threshold of $\sim 3$ keV/Å definitely demonstrates that $(dE/dx)_e$ overwhelms the effect of nuclear collisions.

Enlightenment on the disordering process occurring during heavy-ion irradiation can be obtained on the basis of a phenomenological model developed to account for electrical resistance data recorded on amorphous $Ni_3B$.[14] The assumptions that (i) an incoming ion creates a cylindrical volume of damaged matter along its path with a cross section $s_d$ and (ii) part of the created disorder can be annealed by a subsequent ion impact leading to sample growth allow us to derive a general equation given in Ref. 14. In the particular case of irradiation of a crystalline compound where no growth is evidenced, this general equation can be written as[16]

$$\Delta R/R_0 = \Delta\rho/\rho_0 = r_d[1-\exp(-s_d\Phi)], \quad (1)$$

where $\Phi$ is the irradiation fluence, and $r_d = (\rho_d - \rho_0)/\rho_0$ with $\rho_d$ the resistivity of a damaged region.

The parameters $r_d$ and $s_d$ were determined by fitting the electrical resistance data of Fig. 1 using Eq. (1). Table I collects the values of the different parameters obtained. It has to be noted that the determination of these parameters is unambiguous in the case of Xe irradiation. For Kr and U irradiation, the ion fluence is not high enough for the quantity $s_d\Phi$ to be non-negligible when compared to unity (i.e., for the resistance variation to present an exponential saturation at high fluences as in

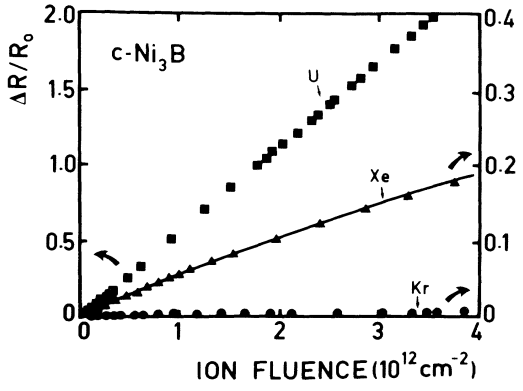


FIG. 1. Relative electrical resistance variation $\Delta R/R_0$ vs ion fluence for crystalline $Ni_3B$ ribbons irradiated at low temperature with various high-energy heavy ions. The solid line is a fit of Eq. (1) to experimental data. Note that the ordinate scale has been multiplied by a factor of 5 for U-irradiation data.

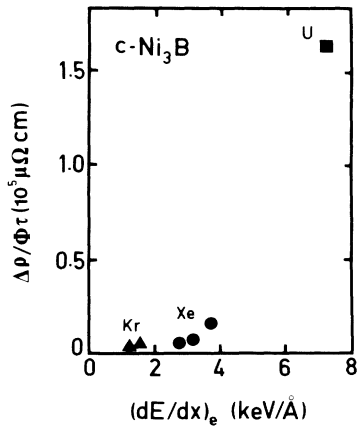


FIG. 2. Initial electrical resistivity variation per elastic DPA vs the ion electronic energy loss for crystalline $Ni_3B$ irradiated at low temperature with high-energy heavy ions.

TABLE I. Parameters extracted from the fit of experimental electrical resistance data by Eq. (1). $\tau$ is the calculated elastic displacement cross section.

| Ion | $(dE/dx)_e$ (keV/Å) | $\tau$ ($10^{-18}$ cm$^2$) | $r_d s_d$ ($10^{-14}$ cm$^2$) | $r_d$ | $s_d$ ($10^{-14}$ cm$^2$) |
|---|---|---|---|---|---|
| Kr | 1.2 | 3.6 | 0.076 | ... | $<0.1$ |
| | 2.8 | 11.1 | 1.0 | 0.33 | 3.0 |
| Xe | 3.2 | 11.2 | 1.6 | 0.32 | 5.0 |
| | 3.7 | 15.6 | 5.7 | 0.57 | 10.0 |
| U | 7.2 | 52.4 | 56 | $>56$ | $<1.0$ |

the case of Xe), so that only the product $r_d s_d$ (corresponding to the initial slope of the resistance increase) can be provided. However, an upper pound of $s_d$ can also be deduced from the resistance data by considering that $s_d \Phi \ll 1$ in this case. The facts that (i) the value of $s_d$ continuously increases with the ion stopping power in the range 1.2–3.7 keV/Å and decreases by almost 1 order of magnitude at higher $(dE/dx)_e$ and (ii) the value of $r_d$ suddenly increases by 1 order of magnitude at 7.2 keV/Å provide a clear indication that a different disordering mechanism takes place above an electronic-energy-loss threshold located between 3.7 and 7.2 keV/Å. The conclusion of amorphous-phase formation at high $(dE/dx)_e$ is then suggested by the observation that the resistivity of the U-irradiated ribbon at the end of the irradiation (44 $\mu\Omega$ cm) is not far from that of its amorphous counterpart (80 $\mu\Omega$ cm) and is still linearly increasing with the U fluence. This conclusion is reinforced by the measurement of the temperature coefficient of the resistivity $[=(1/\rho_{300\,\mathrm{K}})\Delta\rho/\Delta T]$ between 80 and 300 K which exhibits a strong decrease from $2.4\times10^{-3}$ to $1.3\times10^{-3}$ K$^{-1}$ before and after irradiation with U ions. The fraction of amorphized volume in the U-irradiated ribbon has been roughly estimated from the electrical resistance measurements assuming that the resistivity of the crystalline and amorphous phases present in the sample are additive. A value of 30%–40% was thus obtained.

The resistivity results above are fully confirmed by electron microscopy experiments performed on the irradiated samples after annealing at room temperature. While no amorphous regions can be detected on unirradiated samples or after GeV Xe-ion irradiation,[14] electron-diffraction micrographs recorded on the U-irradiated sample, presented in Fig. 3, exhibit the pattern characteristic of a mixture of crystalline and amorphous phases.

The experiments on crystalline $Ni_3B$ irradiated with high-energy heavy ions reported in this paper allow us to draw the main conclusion that electronic energy loss can lead to a crystalline-to-amorphous transition in a metallic alloy. The effect of $(dE/dx)_e$ is clearly ascertained here since the maximum number of elastic DPA induced by irradiation is only $\sim2\times10^{-4}$ while it has been proven that ~0.1 DPA is required for amorphization by nuclear

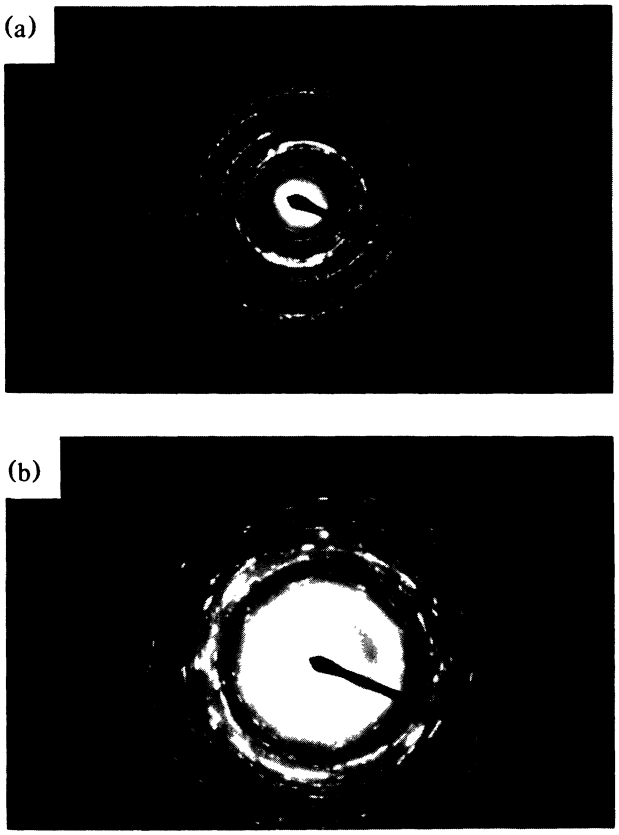


FIG. 3. Transmission-electron-diffraction patterns of a crystalline $Ni_3B$ ribbon (a) before and (b) after irradiation with 3-GeV U ions at a fluence of $4\times10^{12}$ ions cm$^{-2}$. The sample irradiated at 80 K was annealed at room temperature before the observation.

energy loss. The amorphization process by electronic energy loss requires the very high electronic excitation density provided by U irradiation. The linearity of the electrical resistance increase indicates a direct ion-impact mechanism such as that occurring during low-energy heavy-ion irradiation.[17,18] The scenario here could be the following. At very low $(dE/dx)_e$ (Kr irradiation), the damage cross section $s_d$ (which refers to both nuclear and electronic-energy-loss processes) is overwhelmed by elastic collisions. As $(dE/dx)_e$ increases (Xe irradiation), the electronic contribution to $s_d$ increases to become preponderant when compared to the elastic-collision cross section. The core of the ion-damaged region is, however, still not sufficiently disordered to stabilize an amorphous region.[19] Amorphization is then only possible in the case where a tremendous amount of electronic excitation is provided to the irradiated lattice, i.e., by irradiation with a U-ion beam. But even in that case, it is likely that only the core of the damaged track is amorphized, the outer region remaining certainly crystalline although disordered. If such a mechanism is operative, it is clear that the disordering cross section must increase continuously with $(dE/dx)_e$ with a sharp

drop at the onset of amorphization, in agreement with the electrical resistance results presented here.

The difficulty in amorphizing a metallic alloy by ion electronic energy loss can be easily understood by the ability of free electrons to rapidly and efficiently smear out the perturbation caused by the ion beam. The problem is now to identify the mechanism which allows this difficulty to be overcome, i.e., to communicate a sufficient amount of energy to the crystal lattice to produce atomic displacements in the very short time before the conduction electrons screen the perturbation. Two models, respectively based on the thermal-spike and on the Coulomb-explosion concepts, can be invoked to account for the observed ion-beam-induced structural modifications. The former one [20] considers that the kinetic energy of the ejected electrons can be transferred to the target lattice via the electron-phonon interaction, generating a local temperature rise (the so-called thermal spike). In the latter one,[1,7,8] it is assumed that the space charge resulting from the high ionization density along the ion path has a sufficient duration for the ionized atoms to be collectively repelled with an energy high enough to induce atomic displacements. The present experiment does not allow us to give a definite answer concerning the two mechanisms, but for the first time attests that a crystalline-to-amorphous transition can be caused by ion electronic energy loss in a metallic system.

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[15]The case of the U-irradiated ribbon merits an in-depth discussion. Since the final conclusion of the paper is that this sample has been partly amorphized by the U-ion beam, a deformation similar to that occurring in amorphous $Ni_3B$ could be expected during irradiation. Two reasons can be given to explain the nonobservation of this phenomenon: (i) a too weak effect due to the conjunction of the fact that the sample starts out crystalline and is progressively amorphized in the course of irradiation and of the existence of an incubation fluence of a few $10^{12}$ ions cm$^{-2}$ for the growth process; (ii) the possibility that a certain degree of amorphization (higher than the 30%–40% achieved here) is required for the plastic deformation to occur.

[16]It has to be noticed that the absence of measurable growth of the crystalline $Ni_3B$ ribbons during irradiation leads to $\eta=0$ in the general equation of Ref. 14 but does not necessarily imply that the parameters $r_a$ and $s_a$ are also equal to zero. Since, in the present experiment, no data can be derived concerning the values of $r_a$ and $s_a$, Eq. (1) was used in its present form for the sake of simplicity.

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[19]The fact that amorphization of a given volume of a metallic alloy bombarded with energetic ions requires locally a threshold amount of disorder is demonstrated in a large number of resistivity, x-ray, electron-microscopy, and channeling experiments on metal-metalloid and metal-metal compounds irradiated with ions displaying a large variety of cascade geometries (see Refs. 16 and 17). It has, in this respect, to be noted that heavy-ion irradiation was demonstrated to create amorphous clusters by a direct ion-impact mechanism, while amorphization by light-ion or electron irradiation was found to occur by cascade overlapping once a critical level of disorder has been reached.

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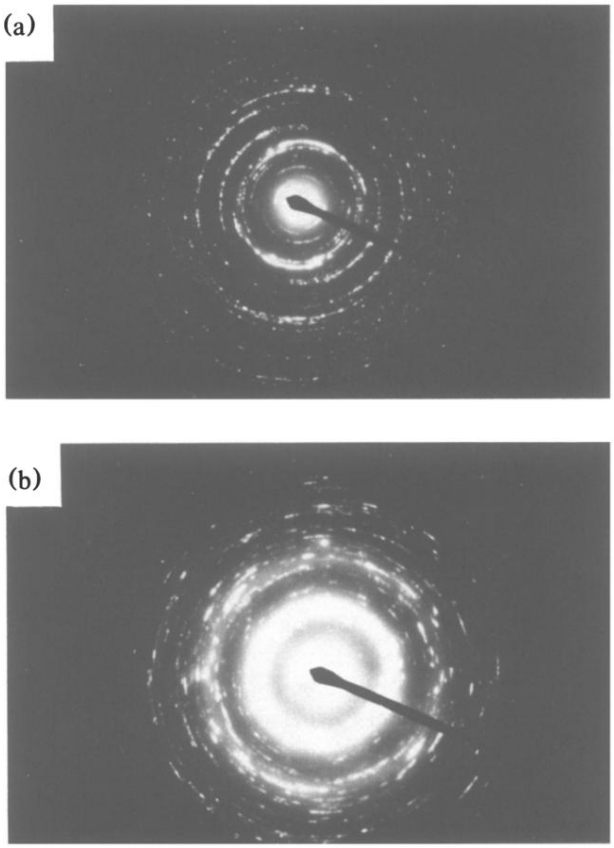


FIG. 3. Transmission-electron-diffraction patterns of a crystalline $Ni_3B$ ribbon (a) before and (b) after irradiation with 3-GeV U ions at a fluence of $4\times10^{12}$ ions cm$^{-2}$. The sample irradiated at 80 K was annealed at room temperature before the observation.