

ANL/MSD/CP--79942

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September 1993

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**INVITED PAPER to be presented at the Eighth International Conference on *Surface Modification of Metals by Ion Beams*, September 13-17, 1993, Kanazawa, Japan.**

**\*Work supported by the U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38.**

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# GENERALIZED MELTING CRITERION FOR BEAM-INDUCED AMORPHIZATION

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## ABSTRACT

Recent studies have shown that the mean-square static atomic displacements provide a generic measure of the enthalpy stored in the lattice in the form of chemical and topological disorder, and that the effect of the displacements on the softening of shear elastic constants is identical to that of heating. This finding lends support to a generalized form of the Lindemann phenomenological melting criterion and leads to a natural interpretation of crystalline-to-amorphous transformations as defect-induced melting of metastable crystals driven beyond a critical state of disorder where the melting temperature falls below the glass-transition temperature. Application of the generalized Lindemann criterion to both the crystalline and amorphous phases indicates that the enthalpies of the two phases become identical when their shear moduli become equal. This thermo-elastic rule provides a basis for predicting the relative susceptibility of compounds to amorphization in terms of their elastic properties as measured by Debye temperatures. The present approach can explain many of the basic findings on beam-induced amorphization of intermetallic compounds as well as amorphous phase formation associated with ion implantation, ion-beam mixing and other solid-state processes.

## 1. Introduction

During the past decade, an increasing number of solid-state techniques has been utilized for producing amorphous metallic alloys. In fact, the crystalline-to-amorphous (c-a) transformations can now be induced by diverse processes ranging from particle beam irradiation, mechanical alloying, hydrogen absorption, to the application of high pressures. Numerous fundamental studies of this phenomenon have been undertaken in recent years [1,2], many of which have focused on electron beam-induced amorphization of intermetallic compounds, in part because of the simple polymorphous nature of the transformation and because the transitions can be studied in situ inside a high-voltage electron microscope. The simple nature of electron damage has also motivated molecular-dynamics (MD) simulations of amorphizing transformations, since only Frenkel pairs and antisite defects are involved and, hence, concepts like thermal spike and local quenching can be neglected. These studies have led to major advances in our understanding of the thermodynamics and kinetics of solid-state amorphization and its relation to the melting process.

Investigations on various ordered intermetallics have revealed a number of important features [3]. A significant early discovery was that the elastic response of intermetallic compounds to structural disordering is very similar to that of heating, namely a progressive softening of the shear modulus related to chemical disordering. This effect was first demonstrated for the  $Zr_3Al$  compound where a 50% decrease in the average shear modulus occurs prior to the onset of amorphization [4,5]. Amorphization takes place when the average shear modulus of the defective compound becomes equal to that of the fully amorphous state. Subsequent work on many different compounds [3] showed that the softening effect is a characteristic feature of c-a transformations and is not observed for compounds which remain crystalline even when chemical long-range order is completely destroyed. To provide atomistic details about the transitions, MD simulations of heat-induced melting and defect-induced amorphization of intermetallic compounds were carried out using realistic interatomic potentials [6-13]. Multislice diffraction theory [14-16] was used to calculate electron diffraction patterns of the atomic configurations generated by the simulations. The computer simulated diffraction patterns exhibited many of the diffraction effects

observed experimentally during irradiation of ordered intermetallic compounds [8,11,12,17]. The MD work provided a quantitative understanding of the relative importance of point defects, chemical disorder, and other possible driving forces for amorphization, and showed that static atomic displacements can be used as a general disorder parameter, i.e., a generic measure of the energy stored in the lattice in the form of chemical and topological disorder. These new insights have been essential in the development of a new approach to solid-state amorphization.

From a diffraction point of view, static atomic displacements in crystalline materials can often be characterized in terms of an artificially-enlarged thermal Debye-Waller factor in which the thermal and static mean-square atomic displacements appear additively. By assuming that this equivalence between thermal and static displacements extends beyond diffraction effects per se, a unified thermodynamic description of solid-state amorphization can be formulated within the framework of a generalized Lindemann melting criterion. This description is well supported by both the results of our molecular dynamics simulations and recent experimental observations of beam-induced amorphization. It will be shown that the Lindemann approach can predict the relative susceptibility of different compounds to amorphization as well as the existence of a critical solute concentration for glass formation by ion implantation or by rapid quenching.

## 2. The Lindemann Approach to Solid-State Amorphization

### 2.1. Generalized Lindemann Melting Criterion

In imperfect crystals, chemical disorder, Frenkel pairs and extended defects can create significant static displacements,  $\langle \mu_{sta}^2 \rangle$ , in addition to displacements resulting from thermal vibrations,  $\langle \mu_{vib}^2 \rangle$ . Recently, we have shown that, by applying the Lindemann phenomenological melting criterion to the total mean-square displacement,  $\langle \mu_T^2 \rangle = \langle \mu_{sta}^2 \rangle + \langle \mu_{vib}^2 \rangle$ , [18] the temperature  $T_d$  at which the defective crystal becomes destabilized (when  $\langle \mu_T^2 \rangle$  exceeds  $\langle \mu_{cri}^2 \rangle$ , a critical value [19]) is given by [8,10-12]

$$T_d = \frac{Mk\theta_d^2}{9\hbar^2} \langle \mu_{cri}^2 \rangle, \quad (1)$$

where  $M$  is the average atomic mass,  $k$  is the Boltzmann constant, and  $\theta_d$  is the Debye temperature of the *defective* crystal, which can be scaled with  $\theta_c$ , the Debye temperature of the *perfect* crystal, in the form

$$\theta_d^2 = \theta_c^2 \left[ 1 - \frac{\langle \mu_T^2 \rangle}{\langle \mu_{cri}^2 \rangle} \right]. \quad (2)$$

Here, the temperature  $T_d$  is expressed in the same form as the original Lindemann relationship between the melting point,  $T_m$ , and  $\theta_c^2$  [20]. However, in contrast to the original version, the Debye temperature and, hence, the 'melting' temperature at constant pressure of the defective crystal are no longer constant; they now decrease linearly with increasing state of disorder as measured by  $\langle \mu_T^2 \rangle$ .

Equations (1) and (2) lead to the following scaling relationship

$$\frac{T_d}{T_m} = \frac{\theta_d^2}{\theta_c^2} = \frac{G_d}{G_c} = 1 - \frac{\langle \mu_T^2 \rangle}{\langle \mu_{cri}^2 \rangle}, \quad (3)$$

with  $G_c$  and  $G_d$  being the average shear elastic constants of the perfect and defective crystals, which are directly proportional to  $\theta_c^2$  and  $\theta_d^2$ , respectively [21]. Thus,

$$\text{for } \langle \mu_T^2 \rangle = 0, \quad \theta_d = \theta_c, \quad G_d = G_c \quad \text{and} \quad T_d = T_m \quad (4)$$

$$\text{and as } \langle \mu_T^2 \rangle \rightarrow \langle \mu_{cri}^2 \rangle, \quad \theta_d \rightarrow 0, \quad G_d \rightarrow 0 \quad \text{and} \quad T_d \rightarrow 0 \quad (5)$$

Equation (5) represents the condition for 'mechanical' melting. However, as discussed in the following section, amorphization can take place via a first-order transition before  $\langle \mu_T^2 \rangle$  reaches  $\langle \mu_{cri}^2 \rangle$ . This can occur when  $\langle \mu_T^2 \rangle = \langle \mu_{cri}^2 \rangle$ , which corresponds to a critical state of disorder analogous to that of 'thermodynamic' melting, where the enthalpy of the defective crystal becomes equal to that of the glassy state (Fig. 1).

## 2.2. Thermo-elastic Criterion for Amorphization

Amorphization becomes thermodynamically possible only if the total increase in enthalpy caused by lattice imperfections exceeds the enthalpy of crystallization, i.e., the enthalpy difference between the amorphous and crystalline states. Application of the generalized Lindemann criterion to these states shows that the enthalpy difference is directly related to the difference in their Debye temperatures. Relative to the perfect crystal, the enthalpy of crystallization can be written as [3]

$$\Delta H_c^0 = L_c \left[ 1 - \frac{\theta_a^2}{\theta_c^2} \right], \quad (6)$$

where  $L_c$  is the pertinent heat of fusion and the subscript 'a' denotes the amorphous state.

The crystallization enthalpy of the defective crystal,  $\Delta H_c^d$ , can also be expressed in the same form as eq. (6) with the subscript 'c' replaced by 'd', so that it scales with  $\Delta H_c^0$  according to

$$\Delta H_c^d = \Delta H_c^0 \left[ \frac{\theta_d^2 - \theta_a^2}{\theta_c^2 - \theta_a^2} \right]. \quad (7)$$

It is clear that  $\Delta H_c^d$  will vanish whenever the defective crystal is driven to a critical state of disorder where its Debye temperature becomes equal to that of the amorphous phase. This condition can be used to define a critical temperature  $T_a$  in the sense that a thermodynamic driving force for amorphization exists below this temperature, where  $\Delta H_c^d$  is negative, but not at higher temperatures (Fig. 1). Application of the Lindemann criterion to the glassy state implies that  $T_a$  is the melting temperature of the glass and, hence, can be interpreted as the glass-transition temperature. Moreover, when combined with eq. (3), eq. (7) shows that

$$\text{as } \langle \mu_T^2 \rangle \rightarrow \langle \mu_{\text{cri}}^2 \rangle^t, \quad \theta_d \rightarrow \theta_a, \quad G_d \rightarrow G_a, \quad \Delta H_c^d \rightarrow 0, \quad \text{and } T_d \rightarrow T_a. \quad (8)$$

This can be considered as the necessary condition for 'thermodynamic' melting of a defective crystal to a glass. However, if the transition is kinetically suppressed for  $\Delta H_c^d \ll 0$ , the 'superheated' defective crystal can be driven to a critical state of disorder where  $\langle \mu_T^2 \rangle = \langle \mu_{\text{cri}}^2 \rangle^m$ , and therefore  $G_d = 0$ , i.e., 'mechanical' melting may occur.

An important consequence of the thermo-elastic criterion for amorphization is that it provides a basis for ranking the tendency of compounds to become amorphous in terms of their elastic properties as measured by Debye temperatures.

### 3. Evidence in Favor of the Generalized Melting Criterion

The generalized melting criterion for solid-state amorphization is supported by both recent MD simulation results and numerous experimental observations.

Computer simulations [6-11] show that compounds can be classified into three groups: type-I compounds can be amorphized either by chemical disorder or by the introduction of Frenkel pairs; type-II compounds are amorphized only by Frenkel pairs; and type-III compounds cannot be amorphized by either type of defects. The MD results also provide considerable insight into the disorder-induced elastic softening effect and why it is so similar to the effect of heating. Some results for NiZr [12,22], a type-I compound, are illustrated in Fig. 2, which shows the effects of isobaric heating, chemical disordering, and Frenkel pairs on the average shear modulus. Presented are plots of  $G_d$  versus  $\Delta V/V$  (relative volume expansion),  $\langle \mu_T^2 \rangle$ , and  $\langle \sigma^2 \rangle$  (mean-square dispersion in the nearest-neighbor distance). The solid arrow on the plot of  $G_d$  versus  $\Delta V/V$  indicates the onset of amorphization in the defective compound while the dashed arrow denotes the volume expansion of the defect-free compound just below its melting point (1400 K). The critical expansions for melting and amorphization are clearly not the same. This finding appears to contradict earlier MD studies on Cu [23], which suggested that the volume dependence of the shear modulus is independent of how the volume expansion is produced. That early result is now recognized to be a consequence of the uniform nature of the expansion process employed in the Cu study. The difference in the critical expansions shown here for NiZr indicates that the volume expansion associated with relaxation of static atomic displacements produces a much larger softening effect than does thermal expansion. This is consistent with the observations on  $Zr_3Al$  where the critical volume expansion for both radiation-induced [4,5] and hydrogen-induced amorphization [24,25] is  $\sim 2.5\%$ , which is about one-half of the typical volume expansion

associated with the ordinary melting process. Thus, volume expansion per se cannot be used as a general disorder parameter for melting and amorphization. However,  $\langle \mu_T^2 \rangle$  satisfies all the requirements of a general criterion for lattice destabilization. In fact, as shown by the plot of  $\langle \mu_T^2 \rangle$  versus  $\Delta V/V$ , the values of  $\langle \mu_T^2 \rangle$  at the two critical expansions are equal. That is, melting (amorphization) of a *defective* crystal occurs whenever  $\langle \mu_T^2 \rangle$  reaches a critical value which is identical to that for melting of the *perfect* crystal. This implies that increasing static atomic disorder is thermodynamically equivalent to heating.

An important corollary is that the melting temperature of a defective crystal must decrease with increasing disorder which, in turn, implies the existence of a critical state of disorder beyond which the melting temperature falls below the glass-transition temperature. The generalized Lindemann criterion therefore leads to a natural interpretation of c-a transformations as melting to a glass of a critically-disordered crystal. The thermodynamic equivalence between disorder and heating is clearly seen in their identical effect on the average shear modulus as shown by the plot of  $G_d$  versus  $\langle \mu_T^2 \rangle$ . This equivalence also holds for Frenkel pairs as shown in the plot of  $G_d$  versus  $\langle \sigma^2 \rangle$ . We use  $\langle \sigma^2 \rangle$ , a quantity which is directly proportional to  $\langle \mu_T^2 \rangle$  [11,12,26], since a direct calculation of  $\langle \mu_T^2 \rangle$  in the case of Frenkel defects is not straightforward, due to the large artificial displacements involved in their creation. The values of  $G_d$  calculated for several compounds, e.g. FeTi, NiZr and NiZr<sub>2</sub>, are plotted versus  $\langle \sigma^2 \rangle$  in Fig. 3. For a direct comparison of the shear softening effect for different alloys, both  $G_d$  and  $\langle \sigma^2 \rangle$  have been normalized to the values of the perfect crystal ( $G_c$ ) and the corresponding liquid ( $\langle \sigma_L^2 \rangle$ ), respectively. The data points obtained for isothermal disorder and isobaric heating lie within a narrow band, indicating that the dependence of  $G_d$  on  $\langle \sigma^2 \rangle$  or  $\langle \mu_T^2 \rangle$  is of a universal nature. The effect of  $\langle \mu_T^2 \rangle$  on the average shear modulus is independent of its physical origin, which implies that  $\langle \mu_T^2 \rangle$  or  $\langle \sigma^2 \rangle$  can represent time or dose, the concentration of point defects, alloy composition, grain size, pressure, or any other measure of disorder. In other words,  $\langle \mu_T^2 \rangle$  or  $\langle \sigma^2 \rangle$  can be used as a universal disorder parameter for both melting and all known types of c-a transformations. The finding that isothermal amorphization and isobaric melting occur whenever  $\langle \sigma^2 \rangle / \langle \sigma_L^2 \rangle$  reaches a critical value

(between 0.5 and 0.6) provides a direct confirmation of the validity of the generalized Lindemann melting criterion.

Recently, Kulp et al. [27] have proposed that the distribution of the atomic-level shear stresses can be used as a criterion for amorphization. They showed that the crystal becomes amorphous when the average shear strain attains a critical value equal to that of the quenched-liquid state. This microscopic criterion is consistent with the present generalized melting criterion.

Figure 4 shows the dose dependence of the Debye temperature  $\theta_d$ , calculated from the average shear modulus  $G_d$  using the well-known expression for isotropic media [28], and its variation with increasing degree of disorder as measured by  $(1 - S^2)$  in NiZr [12,22]. Here,  $S$  is the Bragg-Williams long-range order parameter, and  $(1 - S^2)$  is directly related to the mean-square static displacement [12,22,29].  $\theta_d$  decreases rapidly with increasing dose and, in agreement with experimental observations, becomes equal to  $\theta_a$  at the onset of amorphization. The calculated values of  $\theta_c$  and  $\theta_a$  were  $\sim 315$  and  $200$  K, respectively, in agreement with the reported measurements of  $270$  and  $205$  K [30-32]. In addition, the calculated  $\theta_d^2$  is found to decrease approximately linearly with  $(1 - S^2)$ , reaching the value of the amorphous compound when the c-a transition occurs. These findings are thus in good accord with the predictions of eq. (7).

Experimental support for the generalized Lindemann criterion for melting is provided by various measurements. The connection between a critical mean-square static displacement and the onset of amorphization can be found in recent ion-implantation studies by Linker et al. [33-37]. For example, as B ions were implanted into Nb [33], the average static displacement  $\mu_s$  of the matrix atoms increased rapidly, reaching a maximum value for B concentrations of  $\sim 5$  at.%. Incorporation of interstitial B solutes also led to a simultaneous increase in the lattice parameter and accumulation of strains. The onset of amorphization occurs when  $\mu_s$  attains a critical, maximum value ( $\sim 0.14$  Å) and is accompanied by a significant strain release. Similar features were also demonstrated for the amorphization process in Mn-implanted Al, a substitutional alloy system [36,37]. In this case, however, the lattice parameter decreased linearly with progressive

incorporation of undersized Mn solutes until amorphization set in at a critical concentration of ~8.5 at. % Mn.

The predicted effect of static displacements on the Debye temperature is well supported by recent Brillouin scattering measurements on ion bombarded compounds [3], which showed that the square of the average sound velocity and, hence, the average shear modulus [21] in the defective crystalline compound were linearly decreasing functions of  $(1 - S^2)$ . An example is given in Fig. 5 for  $Kr^+$  bombarded  $Zr_3Al$  [5]. The average shear modulus becomes insensitive to further disorder when  $S$  has reached the critical value at which amorphization occurs. Similarly, in neutron-irradiated  $Mo_3Si$  [38], the squared Debye temperature of the damaged compound  $\theta_d^2$  was found to decrease linearly with increasing  $(1 - S^2)$ . Below a critical state of disorder, corresponding to  $S \approx 0.3$  where  $\theta_d$  becomes equal to  $\theta_a$ , the compound cannot be retained in the crystalline state.

Additional support for the generalized Lindemann criterion comes from the plunging polymorphous melting curves on binary phase diagrams characteristic of easy-glass forming systems. Such curves reflect the  $\langle \mu_T^2 \rangle$  dependence of the polymorphous melting temperature of disordered solid solutions containing misfitting solute atoms. The criterion also predicts the existence of a critical solute concentration for glass formation by rapid quenching, since amorphization can only occur beyond the concentration at which the Debye temperature of the supersaturated solid solution becomes equal to that of the amorphous phase.

According to eq. (7), a compound is expected to be more susceptible to defect-induced amorphization when the difference in the Debye temperature between its crystalline and glassy phases is small. This prediction is confirmed by available measurements. Figure 6A, for example, shows the Debye temperatures measured for pure elements and several ordered compounds [30,31] and amorphous alloys [32,39,40] of the Ni-Zr system. The difference between the Debye temperatures of the crystalline and amorphous states is largest for  $Ni_3Zr$ , intermediate for  $NiZr$  and smallest for  $NiZr_2$ . The critical doses for amorphization of these compounds by electron irradiation were also measured [41] (Fig. 6B). Indeed, the critical electron dose near 0 K was

found to be largest (3.18 dpa) for  $\text{Ni}_3\text{Zr}$ , intermediate (0.37 dpa) for  $\text{NiZr}$  and smallest (0.22 dpa) for  $\text{NiZr}_2$ .

Further support for the thermo-elastic criterion comes from recent HVEM studies [42] showing that pre-doping  $\text{Zr}_3\text{Al}$  with small amounts of hydrogen caused a twenty-five fold reduction in the electron dose needed to amorphize the hydrogen-free compound. We interpret this drastic decrease in critical dose as a consequence of additional static displacements introduced by hydrogen, which reduce the contribution from radiation defects needed for  $\langle \mu_T^2 \rangle$  to reach the critical value.

#### 4. Kinetic Effects

As schematically shown in Fig. 1, the condition  $\theta_d^2 = \theta_a^2$  or  $G_d = G_a$  defines an upper-limiting temperature for amorphization,  $T_a$ , since a thermodynamic driving force for amorphization, i.e.,  $\Delta H_c^d \leq 0$ , exists only for temperatures below  $T_a$ . Based on the generalized Lindemann melting criterion,  $T_a$  is the melting temperature of the amorphous phase, which can also be interpreted as a lower limit of the calorimetrically-determined glass-transition temperature,  $T_g$ . Recent studies of beam-induced amorphization in  $\text{CuTi}$  [43],  $\text{NiAl}$  [44], and  $\text{NiTi}$  [44] showed that  $T_a \simeq 575$ , 240, and 600 K, respectively. In the particular case of  $\text{CuTi}$ ,  $T_a$  is close to the value of ideal  $T_g$ , obtained by extrapolating  $T_g$  data determined by slow, continuous heating of amorphous  $\text{Cu-Ti}$  ribbons [45] to zero heating rate. It is also comparable with the crystallization temperature observed during isochronal annealing of irradiated and unirradiated amorphous  $\text{Cu}_{64}\text{Ti}_{36}$  alloys [46]. Moreover, the  $\text{CuTi}$  work by Koike et al. [43] also revealed a number of important features: (i) at sufficiently low temperatures (below  $\sim 100$  K), the critical dose for amorphization becomes independent of temperature and of the type of irradiating particles; (ii) for any given type of particles, there is a critical temperature  $T^*$  above which the compound cannot be completely amorphized; and (iii) for similar dose rates,  $T^*$  increases with the particle mass, asymptotically approaching the value of  $T_a$ . These observations clearly demonstrate that, in contrast to  $T_a$ ,  $T^*$  is dependent on kinetic effects. For example, the value of  $T^* \simeq 220$  K for electron-induced

amorphization has been shown to be equal to the temperature at which  $S$  abruptly decreases from 1 to  $\sim 0.2$  [47]. According to the Zee-Wilkes model of beam-induced order-disorder transformation [48],  $T^*$  for electron irradiation is determined mainly by the defect production rate and the migration energy of the mobile defects that tend to restore long-range order. For the defect-production rates employed experimentally, Xu [47] has shown that a defect migration energy of  $\sim 0.6$  eV was required to account for the observed  $T^*$ . This value is consistent with the energies of 0.60 - 0.75 eV calculated by molecular statics for vacancy migration across the (002) Ti planes in partially-disordered CuTi compound [49]. Vacancy jumps of this type are responsible for restoring long-range order in CuTi. In contrast to the electron case,  $T^*$  measured for heavy ions such as  $Kr^+$  and  $Xe^+$  has been shown to be the temperature at which small amorphous zones embedded in a crystalline matrix become unstable with respect to crystallization via growth of the crystalline phase, i.e., crystallization without nucleation events [43,50].

#### 4. Conclusion

Various mechanistic aspects of the solid-state amorphizing transformation are summarized in the present paper. By focusing on static atomic displacements as a generic measure of chemical and topological disorder in solids, a unified description of solid-state amorphization was developed on the basis of a generalized form of the well-known Lindemann melting criterion. The generalized version assumes that melting of a defective crystal occurs whenever the sum of the thermal and static displacements reaches a critical value identical to that for melting of the defect-free crystal.

Molecular-dynamics simulations of amorphization and melting showed that the dependence of the average shear modulus on  $\langle \mu_T^2 \rangle$  was identical for isobaric heating to melting of the perfect long-range ordered structure in which  $\langle \mu_T^2 \rangle = \langle \mu_{vib}^2 \rangle$ , and progressive atomic disordering at low temperature where  $\langle \mu_T^2 \rangle \approx \langle \mu_{sta}^2 \rangle$ . For both processes, the average shear modulus decreased essentially linearly with increasing  $\langle \mu_T^2 \rangle$ , and the threshold values of  $\langle \mu_T^2 \rangle$  were the same. These results demonstrate that  $\langle \mu_T^2 \rangle$  provides a direct measure of the potential energy stored in the lattice.

Therefore, it can be used as a generalized disorder parameter in a unified thermodynamic approach to melting and solid-state amorphization. An important prediction of this criterion is that the melting temperature of a defective crystal must decrease with increasing disorder, which, in turn, implies the existence of a critical state of disorder beyond which the melting temperature falls below the glass transition temperature. The generalized Lindemann criterion thus leads to a natural interpretation of c-a transformations as melting to a glass of a critically-disordered crystal. The predicted effect of static displacements on the destabilization of the crystalline structure is supported by various measurements of beam-induced amorphization. Due to its independence of the physical origin of  $\langle \mu_T^2 \rangle$ , the generalized Lindemann melting criterion provides not only the parallel between amorphization and isobaric melting, but also a basic link between the various solid-state amorphizing processes.

### **Acknowledgments**

Our experience in the topic covered in this paper has been acquired in cooperation with a number of colleagues, in particular R. Devanathan, M. Meshii, L. E. Rehn, and M. J. Sabochick. We are indebted to all of them. This work was supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under contract W-31-109-Eng-38.

## References

1. H. Wiedersich and M. Meshii (eds), *Science of Advanced Materials* (ASM International, Metals Park, OH, 1990).
2. D.E. Luzzi (ed), *Solid-State Amorphizing Transformations*, *J. Alloys Comp.* 194 (1993).
3. P.R. Okamoto and M. Meshii, in *Science of Advanced Materials*, edited by H. Wiedersich and M.Meshii (American Society for Metals, Metals Park, OH, 1990) p. 33.
4. L. E. Rehn, P. R. Okamoto, J. Pearson, R. Bhadra, and M. Grimsditch, *Phys. Rev. Lett.* 59 (1987) 2987.
5. P. R. Okamoto, L. E. Rehn, J. Pearson, R. Bhadra and M. Grimsditch, *J. Less Common Met.* 140 (1988) 231.
6. C. Massobrio, V. Pontikis, and G. Martin, *Phys. Rev.* B41, 10486 (1990).
7. M.J. Sabochick and N.Q. Lam, *Phys. Rev.* B43 (1991) 5243.
8. N. Q. Lam, P. R. Okamoto, M. J. Sabochick, and R. Devanathan, *J. Alloys Comp.* 194 (1993) 429.
9. R. Devanathan, N. Q. Lam, M. J. Sabochick, P. R. Okamoto, and M. Meshii, *J. Alloys Comp.* 194 (1993) 447.
10. N. Q. Lam, P. R. Okamoto, R. Devanathan, and M. Meshii, *Proceedings of the NATO Advanced Study Institute on Statics and Dynamics of Alloy Phase Transformations, June 21 - July 3, 1992, Rhodes, Greece* (Plenum Press, New York) in press.
11. R. Devanathan, N. Q. Lam, P. R. Okamoto, and M. Meshii, *Phys. Rev.* B48 (1993) 42.
12. N. Q. Lam, P. R. Okamoto, R. Devanathan, and M. Meshii, *J. Mater. Res.* (submitted).
13. C. Massobrio and V. Pontikis, *Phys. Rev.* B45 (1992) 2484.
14. J. M. Cowley and A. F. Moodie, *Acta Crystallogr.* 10 (1957) 609; 12 (1959) 353.
15. K. Ishizuka and N. Uyeda, *Acta Crystallogr.* A33 (1977) 740.
16. P. A. Stadelmann, *Ultramicroscopy* 21 (1987) 131.
17. R. Devanathan, N. Q. Lam, M. J. Sabochick, P. R. Okamoto, and M. Meshii, *Mater. Res. Soc. Symp. Proc.* 209 (1991) 231.

18. A. Voronel, S. Rabinovich, and A. Kisliuk, *Phys. Rev. Lett.* 60 (1988) 2402.
19. A. Lindemann, *Z. Phys.* 11 (1910) 609.
20. J.M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, Cambridge, 1972) pp. 60-63.
21. G. Grimvall, *Thermophysical Properties of Materials, Selected Topics in Solid State Physics, Vol. XVIII* (North-Holland, Amsterdam, 1986) chapter 4.
22. R. Devanathan, Ph.D. Thesis, Northwestern University, Evanston, IL (1993).
23. D. Wolf, P.R. Okamoto, S. Yip, J.F. Lutsko and M. Kluge, *J. Mater. Res.* 5 (1990) 286.
24. W.J. Meng, P.R. Okamoto, and L.E. Rehn, in *Science of Advanced Materials*, edited by H. Wiedersich and M.Meshii (American Society for Metals, Metals Park, OH, 1990) p. 99.
25. W.J. Meng, J. Faber, P.R. Okamoto, L.E. Rehn, B. J. Kestle, and R. L. Hittermann, *J. Appl. Phys.* 67 (1990) 1312.
26. E. Sevillano, H. Meuth, and J.J. Rehr, *Phys. Rev.* B20 (1979) 4908.
27. D.T. Kulp, T. Egami, D.E. Luzzi, and V. Vitek, *J. Alloys and Compounds* 194 (1993) 417.
28. G. Busch and H. Schade, *Lectures on Solid State Physics* (Pergamon Press, New York, 1976) pp. 61-65.
29. E.V. Kozlov, V.M. Dementryev, V.N. Emelyanov, N.M. Kormin, A.S. Taylashev, and D.M. Stern, in *Order-Disorder Transformation in Alloys*, edited by H. Warlimont (Springer-Verlag, Berlin, 1974) p. 58.
30. A. Amamou, R. Kuentzler, Y. Dossmann, P. forey, J.L. Glimois, and J.L. Feron, *J. Phys. F: Met. Phys.* 12 (1982) 2509.
31. D.G. Onn, L.Q. Wang, Y. Obi, and K. Fukamichi, *Solid State Commun.* 46 (1983) 37.
32. M. Matsuura and U. Mizutani, *J. Phys. F: Met. Phys.* 16 (1986) L183.
33. G. Linker, *Mater. Sci. Eng.* 69 (1985) 105.
34. G. Linker, *Solid State Commun.* 57 (1986) 773.
35. G. Linker, *Nucl. Instrum. Methods* B19-20 (1987) 526.
36. A. Seidel, S. Massing, B. Strehlau, and G. Linker, *Phys. Rev.* B38 (1988) 2273.

37. A. Seidel, G. Linker, and O. Meyer, *J. Less-Common Met.* 145 (1988) 89.
38. A.V. Mermel'shteyn, A.Ye. Kar'kin, V.Ye. Arkhipov, and V.I. Voronin, *Phys. Met. Metall.* 55 (1983) 67.
39. R. Kuentzler, *J. Phys. F: Met. Phys.* 14 (1984) L79.
40. S. Kanemaki, O. Takehira, K. Fukamichi, and U. Mizutani, *J. Phys.: Condens. Matter* 1 (1989) 5903.
41. G. Xu, M. Meshii, P.R. Okamoto, and L.E. Rehn, *J. Alloys Comp.* 194 (1993) 401.
42. W.J. Meng, J. Koike, P.R. Okamoto, and L.E. Rehn, *Mat. Res. Soc. Symp. Proc.* 128 (1989) 345.
43. J. Koike, P.R. Okamoto, R.E. Rehn and M. Meshii, *J. Mater. Res.* 4 (1989) 1143.
44. P. Moine and C. Jaouen, *J. Alloys Comp.* 194 (1993) 373.
45. T.B. Massalski and C.G. Woychik, *Acta Metall.* 33 (1985) 1873.
46. G. Schumacher, S. Klaumünzer, W. Petry, and U. Dedek, *J. Phys. F: Met. Phys.* 18 (1988) 1681.
47. G. Xu, Ph.D. Thesis, Northwestern University, Evanston, IL (1993).
48. R. Zee and P. Wilkes, *Phil. Mag.* 42 (1980) 463.
49. J.R. Shoemaker, R.T. Lutton, D. Wesley, W.R. Wharton, M.L. Oehrli, M.S. Herte, M.J. Sabochick, and N.Q. Lam, *J. Mater. Res.* 6 (1991) 473.
50. J. Koike, Ph.D. Thesis, Northwestern University, Evanston, IL (1989).

## FIGURE CAPTIONS

- FIG. 1: Schematics of the dependence of Debye temperature, average shear modulus, instability temperature, and enthalpy of crystallization on total mean-square atomic displacement, based on the generalized Lindemann melting criterion [10,12].  $\langle\mu_{\text{cri}}^2\rangle^{\text{t}}$  and  $\langle\mu_{\text{cri}}^2\rangle^{\text{m}}$  denote the critical values of  $\langle\mu_1^2\rangle$  for *thermodynamic* and *mechanical* melting, respectively.
- FIG. 2: Plots of the average shear modulus,  $G_{\text{d}}$ , versus the volume expansion,  $\Delta V/V$ , total mean-square atomic displacement,  $\langle\mu_1^2\rangle$ , and mean-square dispersion in the nearest-neighbor distance,  $\langle\sigma^2\rangle$ , in NiZr [12,22]. The variation of  $\langle\mu_1^2\rangle$  with  $\Delta V/V$  is also shown for the cases of isobaric melting and chemical disordering. The solid and dashed arrows indicate the onset of amorphization in the defective compound and the state of the defect-free crystal just below its melting point (1400 K), respectively.
- FIG. 3: Variation of the average shear modulus with the mean-square dispersion in the nearest-neighbor distance in FeTi, NiZr, and NiZr<sub>2</sub> [11,12,22]. The shear modulus  $G_{\text{d}}$  has been normalized to the value obtained for the perfect crystal,  $G_{\text{e}}$ , and  $\langle\sigma^2\rangle$  normalized to its value in the liquid slightly above the melting point,  $\langle\sigma_{\text{L}}^2\rangle$ .
- FIG. 4: Dependence of the Debye temperature on damage dose and  $(1 - S^2)$  calculated for NiZr [12,22]. The experimental values for the undamaged crystalline compounds [30] and glassy alloys [31] are indicated.
- FIG. 5: Decrease of the average sound velocity with increasing state of disorder  $(1 - S^2)$  in 1-MeV Kr<sup>+</sup> bombarded Zr<sub>3</sub>Al. After Okamoto et al. [5].
- FIG. 6: (A) Compositional dependence of the Debye temperature measured for the Ni-Zr alloy system. Data for pure elements and ordered compounds are taken from refs. 30 and 39, and data for amorphous alloys from refs. 31,32 and 40. (B) Temperature dependence of the critical dose for amorphization of NiZr, NiZr<sub>2</sub>, and Ni<sub>3</sub>Zr. After Xu et al. [41].

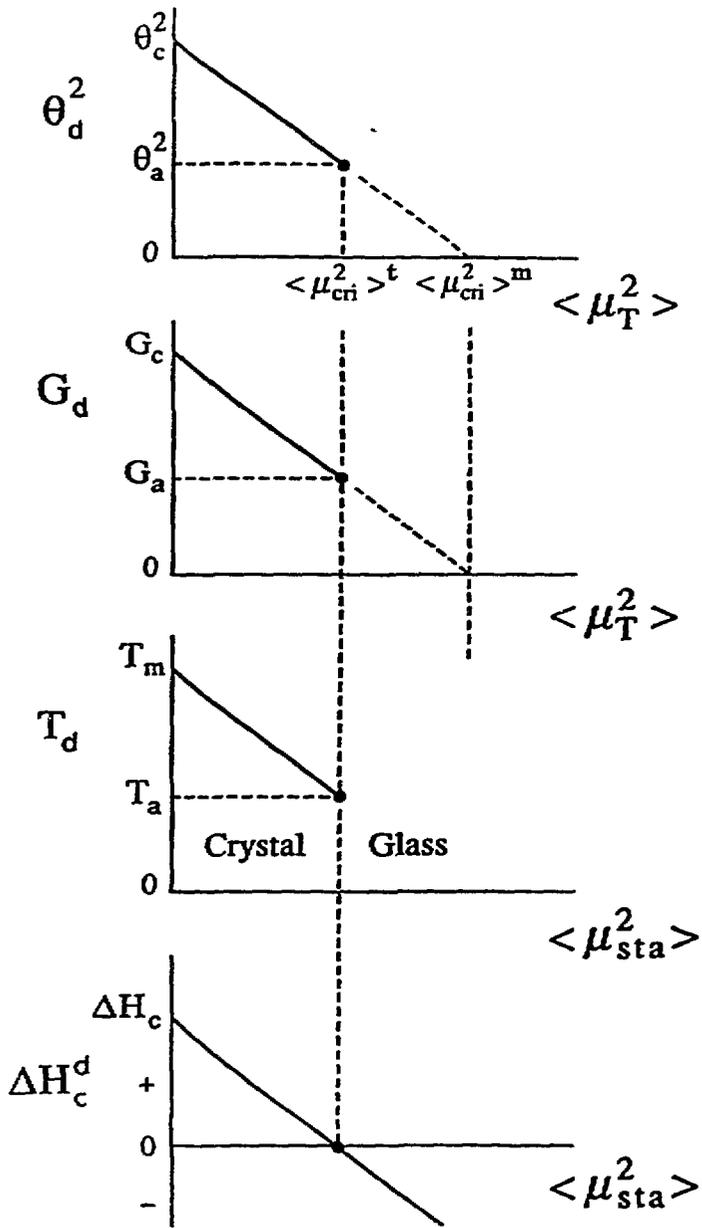


Fig. 1

# NiZr

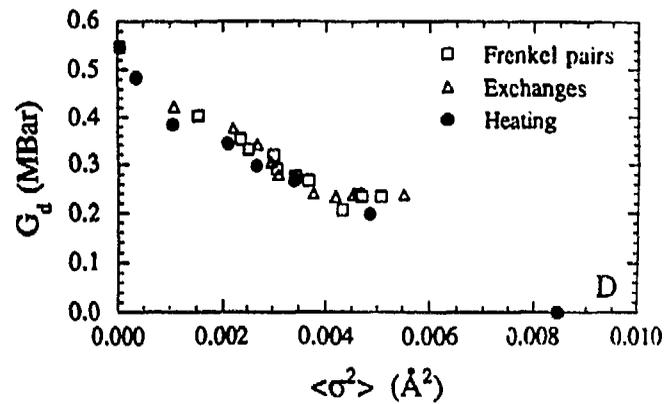
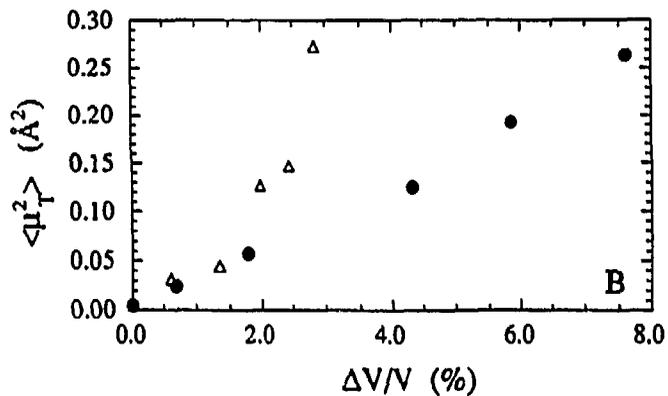
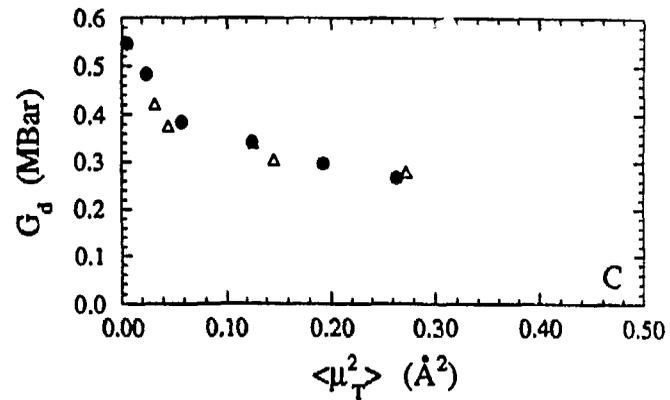
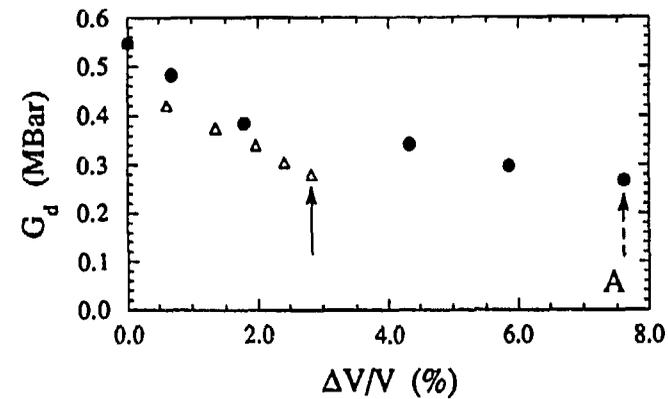


Fig. 2

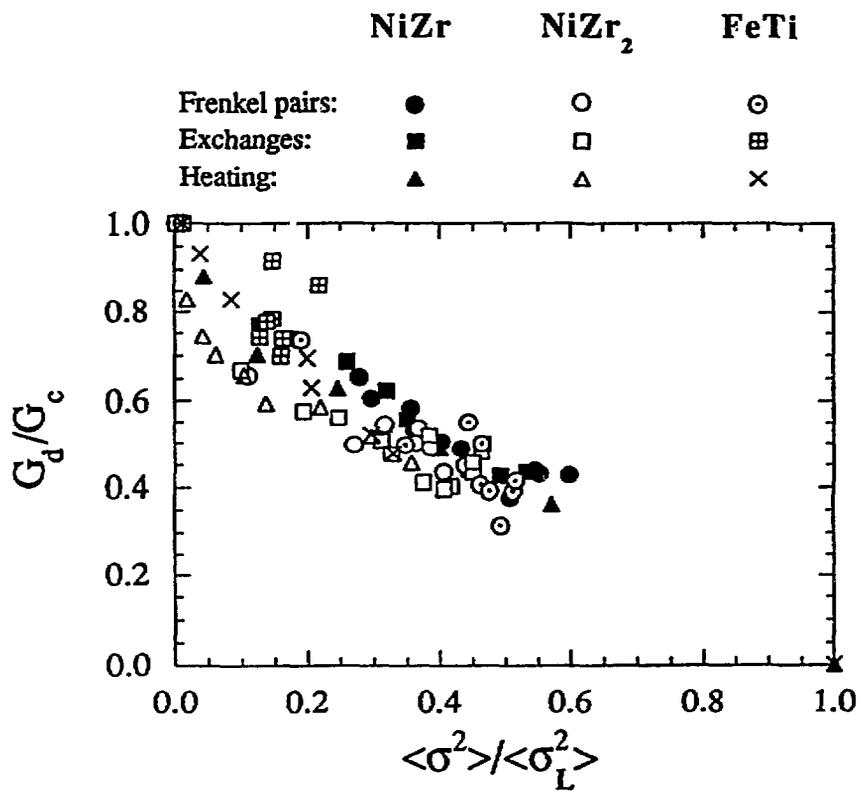


Fig. 3

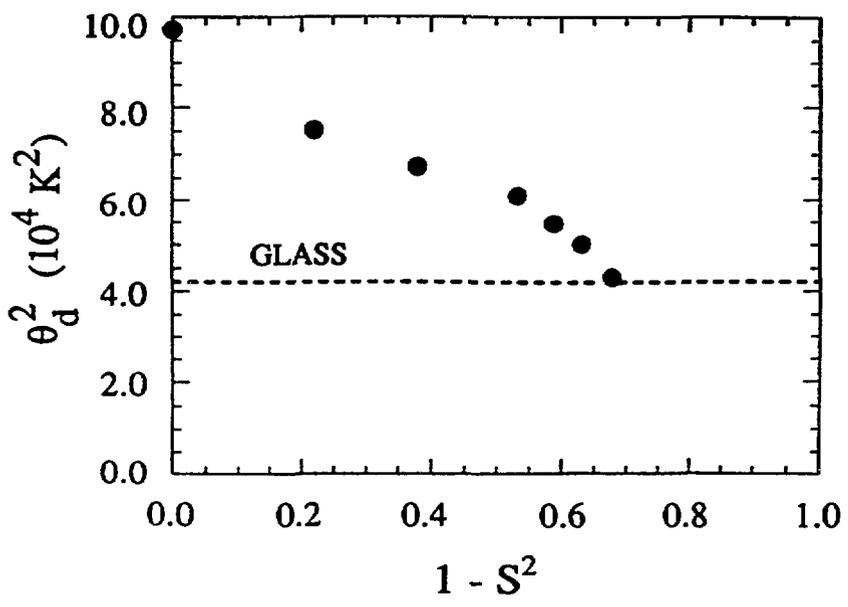
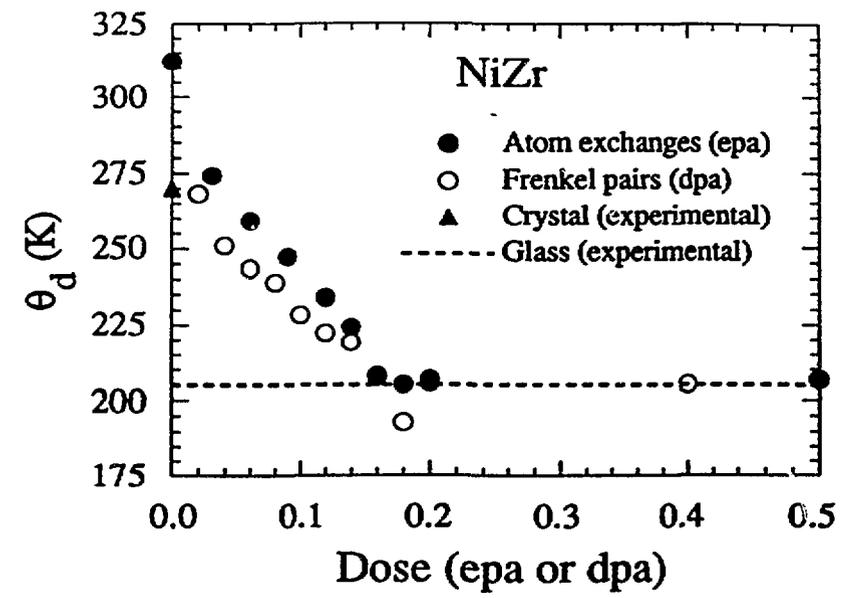


Fig. 4

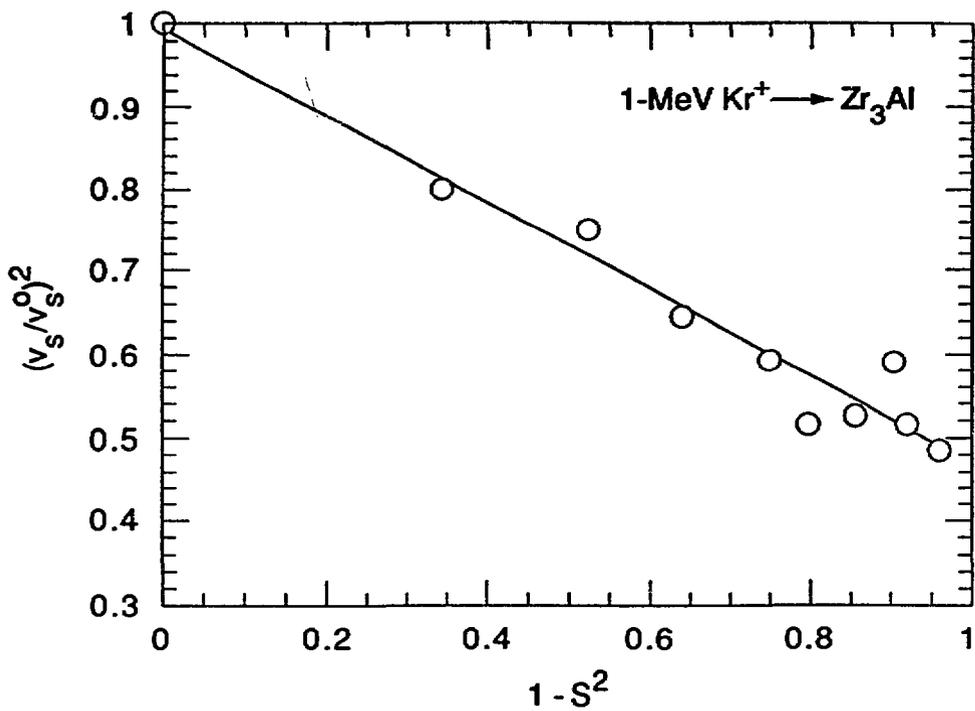


Fig. 5

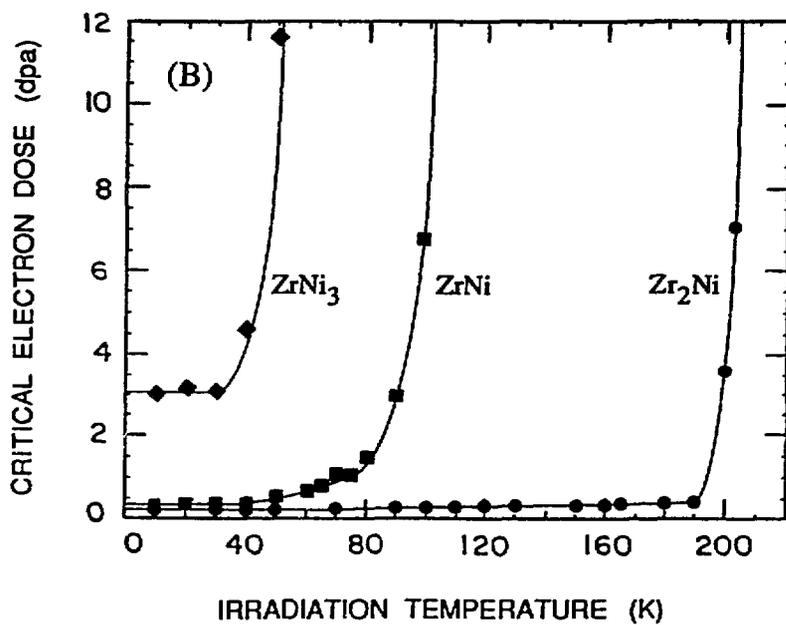
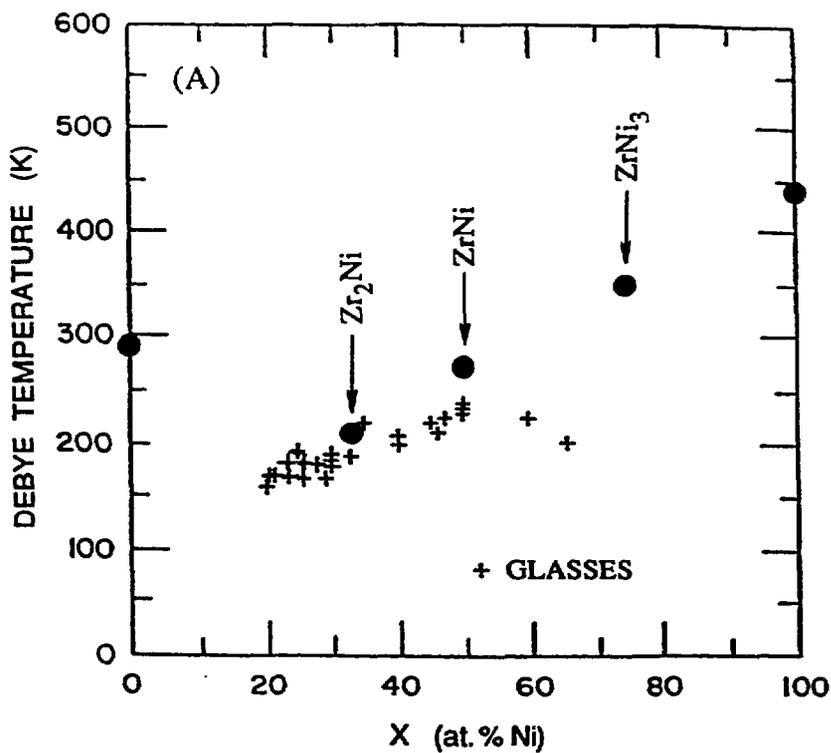


Fig. 6