

CONF-921101--59

## GENERALIZED MELTING CRITERION FOR AMORPHIZATION\*

R. Devanathan<sup>1,2</sup>, N. Q. Lam<sup>1</sup>, P. R. Okamoto<sup>1</sup> and M. Meshii<sup>2</sup>

<sup>1</sup>Materials Science Division, Argonne National Laboratory  
Argonne, IL 60439

<sup>2</sup>Dept. of Materials Science and Engineering, Northwestern University  
Evanston, IL 60208

ANL/MSD/CP--76615

DE93 005557

December 1992

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

Received by OSTI

JAN 08 1993

Submitted to the 1992 Materials Research Society Fall Meeting, November 30-December 4, 1992, Boston, MA.

\*Work supported by the U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38 and NSF Grant DMR-8802847.

**MASTER**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *zb*

# GENERALIZED MELTING CRITERION FOR AMORPHIZATION

R. DEVANATHAN<sup>1,2</sup>, N. Q. LAM<sup>1</sup>, P. R. OKAMOTO<sup>1</sup> and M. MESHII<sup>2</sup>

<sup>1</sup> Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

<sup>2</sup> Dept. of Materials Science and Engineering, Northwestern University, Evanston, IL 60208

## ABSTRACT

We present a thermodynamic model of solid-state amorphization based on a generalization of the well-known Lindemann criterion. The original Lindemann criterion proposes that melting occurs when the root-mean-square amplitude of thermal displacement exceeds a critical value. This criterion can be generalized to include solid-state amorphization by taking into account the static displacements. In an effort to verify the generalized melting criterion, we have performed molecular dynamics simulations of radiation-induced amorphization in NiZr, NiZr<sub>2</sub>, NiTi and FeTi using embedded-atom potentials. The average shear elastic constant  $G$  was calculated as a function of the total mean-square atomic displacement following random atom-exchanges and introduction of Frenkel pairs. Our results provide strong support for the generalized melting criterion.

## INTRODUCTION

Over the past three decades, extensive studies have been performed in an effort to understand solid-state amorphizing transformations. Many of these studies have focussed on radiation-induced amorphization [1], which represents a destabilization of the crystalline lattice caused by particle bombardment at temperatures well below the melting point. In particular, electron irradiation-induced amorphization has attracted considerable interest because it results in simple damage, and can be studied *in situ* in a high voltage electron microscope (HVEM). In addition to HVEM experiments, molecular dynamics simulations have been employed to understand the mechanism of amorphization [2-6]. These simulations have shed new light on the atomistic details of the amorphization process. They have also brought forth evidence indicating the existence of parallels between melting and solid-state amorphization. In this report, we present a generalized melting criterion that offers a unified picture of melting and solid-state amorphization.

## CHARACTERISTICS OF AMORPHIZATION

Irradiation by MeV electrons produces Frenkel pairs and chemical disorder. The relative importance of these two defects to the amorphization process has been a contentious issue [7-9]. In order to understand the mechanism of amorphization, we have performed molecular dynamics simulations using embedded-atom potentials in NiZr, NiZr<sub>2</sub>, FeTi and NiTi. Details of the simulations and the interatomic potentials can be found elsewhere [3-5]. The behavior of the compounds that undergo amorphization fall into two distinct classes, which are represented by NiZr<sub>2</sub> and FeTi. In this section, we will discuss the changes in properties of NiZr<sub>2</sub> and FeTi with Frenkel pair introductions and random atom exchanges. The doses for these two types of damage are in displacements per atom (dpa) and exchanges per atom (epa), respectively.

Figure 1 shows the changes in the potential energy increase per atom  $\Delta E/N$ , volume expansion  $\Delta V/V$  and average shear elastic constant  $G$  (average of  $C_{44}$  and  $C'$ ) as functions of dose for NiZr<sub>2</sub> and FeTi. In NiZr<sub>2</sub>, for the case of exchanges as well as Frenkel pairs, the energy and volume increase monotonically with damage dose and saturate at the level of the

quenched liquid (indicated by the dotted line). Correspondingly, the average shear elastic constant decreases by about 50%. At this point  $C_{44}$  and  $C'$  become equal (not shown here), indicating the attainment of elastic isotropy. These property changes along with the structural changes (not shown) indicate that  $\text{NiZr}_2$  can be amorphized by Frenkel pairs or chemical disorder. The same is also true of  $\text{NiZr}$ . On the other hand,  $\text{FeTi}$  can be amorphized by Frenkel pair introduction but not by chemical disorder. The behavior of the properties of  $\text{FeTi}$  with displacement damage is similar to that seen in  $\text{NiZr}_2$ . However, with exchanges, the energy and volume saturate at values far below those of the quenched liquid, and the decline in the average shear elastic constant is smaller. Moreover,  $C_{44}$  and  $C'$  do not become equal, that is, elastic isotropy is never attained. Thus,  $\text{FeTi}$  can be amorphized by Frenkel pair introduction but not by chemical disorder. This behavior is also exhibited by  $\text{NiTi}$ ,  $\text{CuTi}$  and  $\text{Cu}_4\text{Ti}_3$  [5].

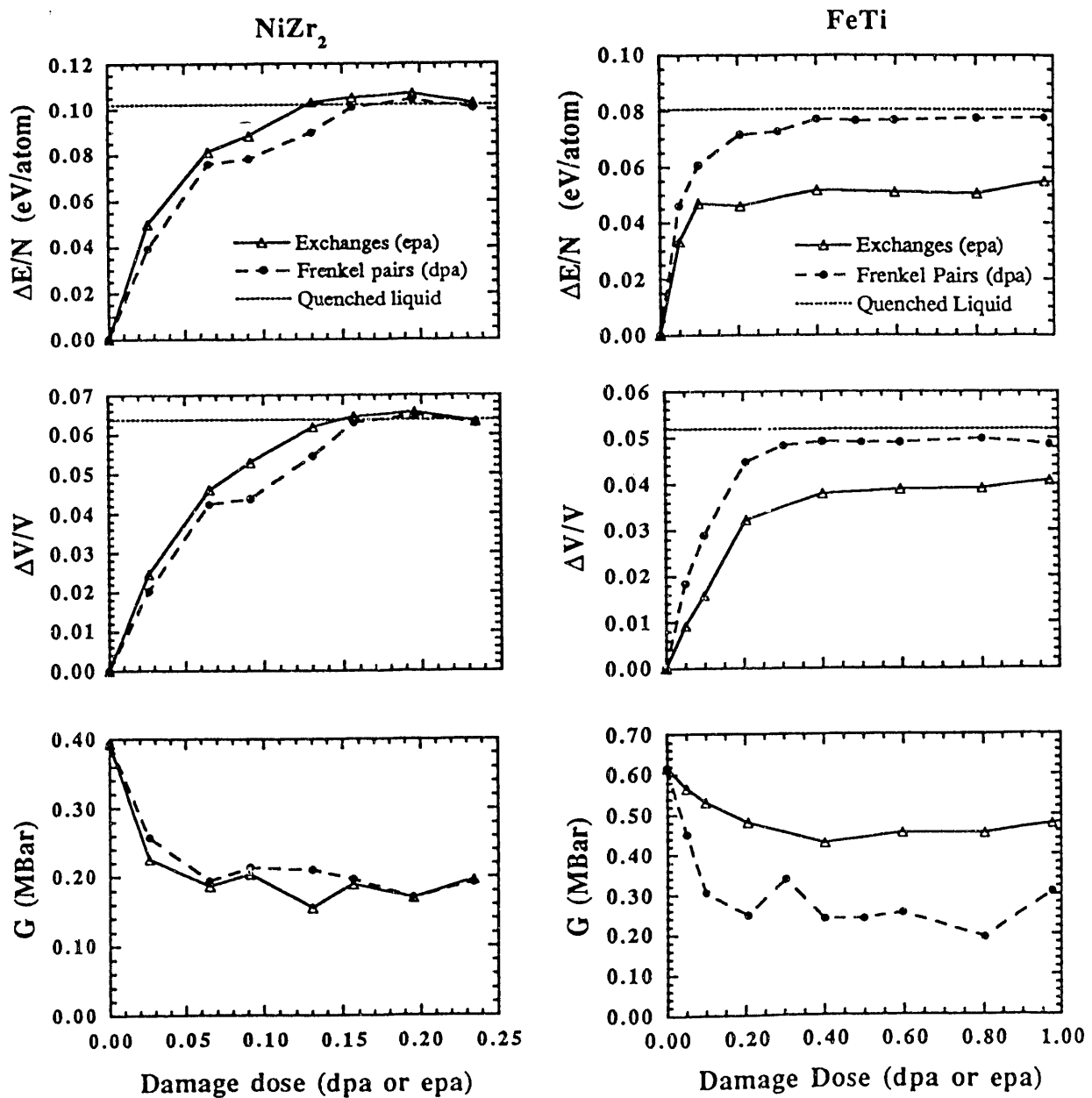


Fig. 1 Changes in the thermodynamic and mechanical properties of  $\text{NiZr}_2$  and  $\text{FeTi}$  with dose.

It is clear from the above that generalizations about the importance of one defect or the other in bringing about amorphization cannot be made. Different mechanisms can operate in different compounds, and even within a given alloy system. Our simulations show that in all the compounds studied, following Frenkel pair introduction, most of the vacancies recombine with interstitials and create chemical disorder. Therefore, it is evident that chemical disorder is responsible for much of the energy increase during electron irradiation. In some compounds, such as FeTi, NiTi, CuTi and Cu<sub>4</sub>Ti<sub>3</sub>, this energy increase is insufficient to cause amorphization. The extra energy needed to amorphize the material is supplied by Frenkel pairs that survive recombination. Lam *et al.* [5] have shown that in Cu<sub>4</sub>Ti even this extra energy is insufficient to drive the compound amorphous. Such compounds cannot be amorphized by electron irradiation. This is borne out by experimental evidence [1]. However, it is not clear why different compounds within the same system, such as CuTi and Cu<sub>4</sub>Ti, behave differently under electron irradiation. In order to account for this difference and to understand the elastic softening prior to amorphization, we have formulated a generalized melting criterion [5,6].

## GENERALIZED MELTING CRITERION

Lindemann [10] has proposed that an ideal crystal melts when the root-mean-square amplitude of thermal vibrations,  $\langle \mu_{\text{vib}}^2 \rangle^{1/2}$ , exceeds a critical value  $\langle \mu_{\text{cri}}^2 \rangle^{1/2}$ . The mechanical melting temperature  $T_m$  of a perfect crystal is related to  $\langle \mu_{\text{cri}}^2 \rangle$  by [11]

$$T_m = \frac{Mk\Theta_c^2}{9h^2} \langle \mu_{\text{cri}}^2 \rangle \quad (1)$$

where  $\Theta_c$  is the Debye temperature of the perfect crystal,  $M$  is the atomic mass, and  $k$  is the Boltzmann constant. In the case of defective solids, lattice defects such as chemical disorder and Frenkel pairs can give rise to an additional static component,  $\langle \mu_{\text{sta}}^2 \rangle$ , to the mean-square atomic displacement. Voronel *et al.* [12] have pointed out that the Lindemann criterion should be applied to the total mean square displacement  $\langle \mu_{\text{T}}^2 \rangle$ , which, by assuming statistical independence, is the sum of  $\langle \mu_{\text{vib}}^2 \rangle$  and  $\langle \mu_{\text{sta}}^2 \rangle$ :

$$\langle \mu_{\text{T}}^2 \rangle = \langle \mu_{\text{vib}}^2 \rangle + \langle \mu_{\text{sta}}^2 \rangle \quad (2)$$

A defective crystal can thus be destabilized at a temperature  $T_d$  given by

$$T_d = \frac{Mk\Theta_d^2}{9h^2} \langle \mu_{\text{cri}}^2 \rangle \quad (3)$$

where  $\Theta_d$ , the Debye temperature of the defective crystal, is defined as

$$\Theta_d^2 = \Theta_c^2 \left[ 1 - \frac{\langle \mu_{\text{sta}}^2 \rangle}{\langle \mu_{\text{cri}}^2 \rangle} \right] \quad (4)$$

Equations (1), (3) and (4) lead to the following scaling relationships :

$$\frac{T_d}{T_m} = \frac{\Theta_d^2}{\Theta_c^2} = \frac{G_d}{G_c} = 1 - \frac{\langle \mu_{sta}^2 \rangle}{\langle \mu_{cri}^2 \rangle} \quad (5)$$

with  $G_c$  and  $G_d$  being the average shear elastic constants of the unirradiated and defective crystals, respectively. Thus

$$\text{as } \langle \mu_{sta}^2 \rangle \rightarrow 0, \quad \Theta_d \rightarrow \Theta_c, \quad G_d \rightarrow G_c, \quad \text{and} \quad T_d \rightarrow T_m \quad (6)$$

$$\text{and as } \langle \mu_{sta}^2 \rangle \rightarrow \langle \mu_{cri}^2 \rangle, \quad \Theta_d \rightarrow 0, \quad G_d \rightarrow 0, \quad \text{and} \quad T_d \rightarrow 0 \quad (7)$$

The last condition corresponds to mechanical melting. Generally, however,  $G_d$  need not vanish because amorphization can occur via a first-order transition before  $\langle \mu_T^2 \rangle$  reaches  $\langle \mu_{cri}^2 \rangle$ , i.e., when  $\langle \mu_T^2 \rangle$  equals  $\langle \mu_{cri}^2 \rangle$ . This corresponds to a critical state of disorder when thermodynamic melting takes place [6].

The enthalpy difference between the defective crystal and the amorphous state is given by [1]

$$\Delta H_c = L_d \left[ 1 - \frac{\Theta_a^2}{\Theta_d^2} \right] \quad (8)$$

where  $\Theta_a$  is the Debye temperature of the amorphous material and  $L_d$  is the heat of fusion of the crystalline material. When combined with eq. (5), eq. (8) shows that

$$\Delta H_c \rightarrow 0 \quad \text{when} \quad \langle \mu_T^2 \rangle \rightarrow \langle \mu_{cri}^2 \rangle, \quad \text{such that} \quad \Theta_d \rightarrow \Theta_a, \quad G_d \rightarrow G_a \quad \text{and} \quad T_d \rightarrow T_a \quad (9)$$

The subscript 'a' denotes quantities corresponding to the amorphous state. Since the enthalpy difference vanishes, eq. (9) can be interpreted as the necessary condition for 'thermodynamic' melting of a defective crystal. It follows that amorphization is possible only if  $T_d = T_a \leq T_g$ , with  $T_g$  being the glass transition temperature. However, if amorphization is kinetically suppressed, mechanical melting will take place when  $\langle \mu_T^2 \rangle$  reaches  $\langle \mu_{cri}^2 \rangle$ . In the following section, we present more evidence in favor of the generalized melting criterion.

## SIMULATION RESULTS

Figure 2 shows plots of the normalized average shear elastic constant,  $G_d/G_c$  for NiZr, NiZr<sub>2</sub>, FeTi and NiTi as functions of the mean-square displacement normalized to the mean-square atomic displacement (non-diffusional) in the liquid state at the melting temperature

$\langle \mu_T^2 \rangle / \langle \mu_{cri}^2 \rangle$ . The plots are shown for three processes, namely, heating upto melting, Frenkel pair introduction and random exchanges. We have assumed  $\langle \mu_{vib}^2 \rangle = \langle \mu_T^2 \rangle$  for the heating of a perfect crystal and  $\langle \mu_{sta}^2 \rangle = \langle \mu_T^2 \rangle$  for Frenkel pairs and exchanges (performed at 30 to 160 K) because these are, respectively, the dominant components of atomic displacement. The displacement was determined from the deviation of the average nearest-neighbor arrangement from that in the perfect crystal. This technique was adopted to avoid the large artificial displacements produced during random Frenkel pair introduction, and maintain consistency for the sake of comparison between the measurements in the three processes. The details of the calculation are given elsewhere [13].

For all four compounds,  $G_d/G_c$  saturates at about 0.4 following Frenkel pair introduction. This corresponds to a  $\langle \mu_T^2 \rangle / \langle \mu_{cri}^2 \rangle$  of 0.5 to 0.6. At this point, amorphization takes place, and no further increase in  $\langle \mu_T^2 \rangle / \langle \mu_{cri}^2 \rangle$  is observed when the displacement dose is increased. Random atom exchanges have a similar effect in NiZr and NiZr<sub>2</sub>, which are amorphized by chemical disorder at  $S \approx 0.5$ . However, in NiTi and FeTi,  $\langle \mu_T^2 \rangle / \langle \mu_{cri}^2 \rangle$  does not increase beyond 0.35 and 0.2, respectively, even for the case of complete chemical disorder ( $S=0$ ). In all four compounds, the variation of  $G_d/G_c$  with  $\langle \mu_T^2 \rangle / \langle \mu_{cri}^2 \rangle$  is consistent with the generalized Lindemann criterion. This criterion also explains the differences in susceptibility to

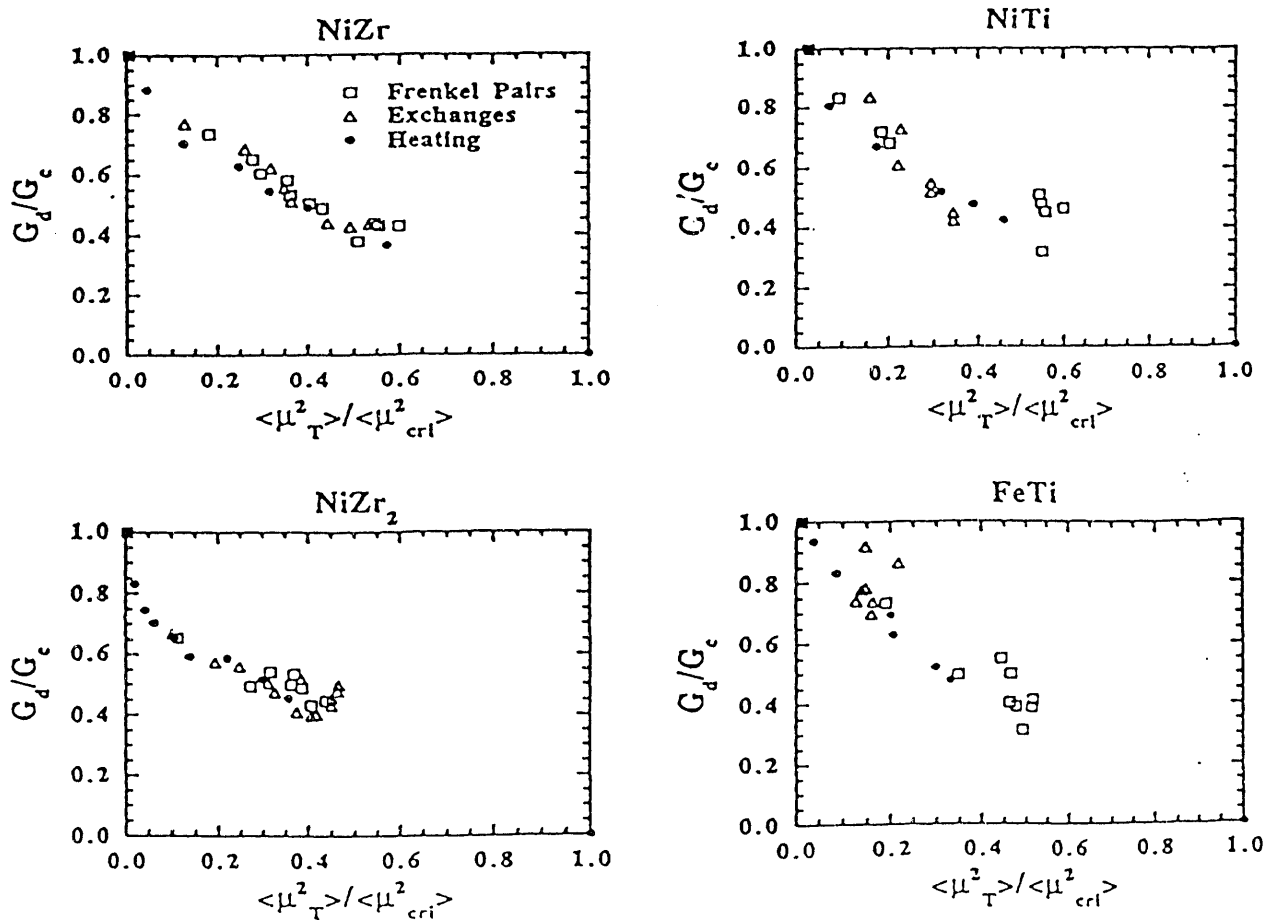


Fig.2. Variation of  $G_d/G_c$  with  $\langle \mu_T^2 \rangle / \langle \mu_{cri}^2 \rangle$  for NiZr, NiZr<sub>2</sub>, NiTi and FeTi

amorphization among compounds of the same system, e.g., CuTi and Cu<sub>4</sub>Ti. Amorphization is easier when the crystallization enthalpy is smaller, i.e., for a smaller difference in the Debye temperatures between the crystalline and amorphous states, according to eq. (8). Evidence in favor of this correlation was recently obtained for Ni-Zr compounds by Xu *et al.* [14].

## CONCLUSIONS

We have proposed a thermodynamic description of solid-state amorphization based on the idea that the crystal is destabilized when the total mean-square displacement exceeds a critical value. This criterion is confirmed by recent experimental observations, and the results of our molecular dynamics simulations of electron irradiation effects in several intermetallic compounds.

## ACKNOWLEDGEMENTS

This work was supported by U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38 and NSF Grant DMR-8802847. It has benefitted from a grant of time on the Cray supercomputers at NERSC, Lawrence Livermore National Laboratory. The authors thank Dr. M. J. Sabochick for several stimulating discussions.

## REFERENCES

1. P. R. Okamoto and M. Meshii, in *Science of Advanced Materials*, edited by H. Wiedersich and M. Meshii (ASM, Metals Park, OH, 1990), pp. 33-98.
2. C. Massobrio, V. Pontikis and G. Martin, *Phys. Rev. B* **41**, 10486 (1990).
3. M. J. Sabochick and N. Q. Lam, *Phys. Rev. B* **43**, 5243 (1991); *Mat. Res. Soc. Symp. Proc.* **201**, 387 (1991).
4. R. Devanathan, N. Q. Lam, M. J. Sabochick, P. R. Okamoto and M. Meshii, *J. Alloys and Compounds* (in press); *Mat. Res. Soc. Symp. Proc.* **235**, 539 (1992).
5. N. Q. Lam, P. R. Okamoto, M. J. Sabochick and R. Devanathan, *J. Alloys and Compounds* (in press).
6. 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).
7. H. Mori and H. Fujita, *Jpn. J. Appl. Phys.* **21**, L494 (1982).
8. Y. Limoge and A. Barbu, *Phys. Rev. B* **30**, 2212 (1984).
9. D. E. Luzzi and M. Meshii, *Res Mechanica* **21**, 207 (1987).
10. A. Lindemann, *Z. Phys.* **11**, 609 (1910).
11. J. M. Ziman, *Principles of the Theory of Solids*, Cambridge University Press, Cambridge (1972), p. 65.
12. A. Voronel, S. Rabinovich, A. Kisliuk, V. Steinberg and T. Sverbilova, *Phys. Rev. Lett.* **60**, 2402 (1988).
13. R. Devanathan, N. Q. Lam, M. J. Sabochick, P. R. Okamoto and M. Meshii, (to be published).
14. G. Xu, M. Meshii, P. R. Okamoto and L. E. Rehn, *J. Alloys and Compounds* (in press).

**END**

---

**DATE  
FILMED  
3 / 8 / 93**

