

## Zirconium nitride—a new material for Josephson junctions

K. Schwarz,\* A. R. Williams, J. J. Cuomo, J. H. E. Harper,  
and H. T. G. Hentzell†

IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York, 10598

(Received 2 July 1985)

ZrN in the NaCl structure is a superconductor with a  $T_c$  of 10 K. With use of an ion-beam process, nitride with higher nitrogen composition than NaCl can be deposited, which is found to be an insulator. A similar situation is found for the Hf but not for the Ti nitride. For this insulator an ordered defect structure  $Zr_3N_4$  is suggested. An octet rule could make this compound an insulator. Augmented-spherical-wave (ASW) band-structure calculations are performed and yield a significant lowering of the Fermi energy with respect to ZrN (NaCl), but a small overlap between the N  $p$  and Zr  $d$  bands remains. Although these calculations, which are based on the local-density approximation, yield conduction and valence bands that overlap slightly, the fundamental origin of the insulating behavior appears to be quite clear. If Ne is implanted in the void, the insulator  $NeZr_3N_4$  has a lattice spacing which perfectly matches that of the superconductor ZrN (NaCl) as predicted by ASW calculations and confirmed experimentally. A Josephson junction built with these isochemical and isostructural materials should have a perfect match at the interface.

### I. INTRODUCTION

The refractory transition-metal compounds, especially the carbides and nitrides such as TiC, TiN or NbC, NbN are a very interesting class of materials, because they combine various physical and chemical properties such as high melting points (around 3000°C) and ultrahardness (comparable to diamond), but exhibit metallic conductivity at the same time. Some of these materials are superconductors with a  $T_c$  as high as 18 K (for example, the carbonitride of Nb).

In this paper we first discuss the electronic properties of several refractory metal compounds, especially ZrN (Sec. II); then we describe new experiments in which insulating "higher-[N] nitrides" (with a higher nitrogen composition than in NaCl) have been obtained (Sec. III). For this insulator an ordered structure is suggested, e.g.,  $Zr_3N_4$  whose electronic properties are studied by augmented-spherical-wave (ASW) band-structure calculations (Sec. IV). Total energy minimization yields equilibrium lattice constants which are very similar for the superconducting and insulating forms of zirconium nitride so that these two—in terms of the interface—could be an ideal material for building Josephson-junction devices (Sec. V).

### II. ELECTRONIC STRUCTURE OF REFRACTORY METAL COMPOUNDS

#### A. Carbides and nitrides crystallizing in the NaCl structure

Since the refractory metal compounds are of great technological interest, they have been studied extensively (for a review, see Calais<sup>1</sup>). Many of the theoretical investigations of those compounds, which crystallize in the NaCl structure, have been carried out in Vienna<sup>2-5</sup> and are

described in a recent review by Neckel.<sup>6</sup> In these calculations the augmented-plane-wave (APW) method has been used and they yield energy bands, the corresponding state densities, and electron densities, quantities from which valuable information on the bonding can be obtained. It is found that all three main types of bonding contribute in the refractories: (i) *metallic* contributions with a finite density of states at the Fermi energy; (ii) *ionic* bonding caused by a charge transfer from the metal to the nonmetal atom; (iii) *covalent* bonds, in particular, a strong interaction between the nonmetal  $p$  and the metal  $d$  valence states, but also metal-metal interactions. The covalent component is strongest in the carbides, it is weaker in the nitrides, but it is much reduced in the related oxides.

Although in such a series the reduction in covalency is accompanied by an increase in ionicity, the charge transfer remains about constant or even slightly decreases, an observation which can be understood from the density-of-states data.<sup>2</sup> Recently the binding mechanism of the series TiC, TiN, and TiO was discussed in detail by Blaha and Schwarz.<sup>5</sup> If we take TiC as an example, the pronounced stability, i.e., the hardness or the high melting point, can be qualitatively understood by observing that the Fermi energy falls in a pronounced minimum of the density of states (DOS). In terms of the Ti  $d$ -C  $p$  interaction all bonding states are occupied while the antibonding states remain unoccupied.

Nonstoichiometry effects are particularly important in these compounds, because they strongly affect the properties of these materials. As yet, mainly vacancies on the nonmetal sublattice have been studied, since these often destroy superconductivity.<sup>7-11</sup> Lattice relaxations around the nonmetal vacancies have been found to be important, for example, when high-precision x-ray-diffraction measurements of the valence-electron distribution in  $TiC_{0.94}$  have been analyzed.<sup>12,13</sup>

### B. ZrN

We now turn to ZrN, a superconductor with a  $T_c$  of about 10 K. Its electronic structure has been described before<sup>4</sup> and consists of a low-lying N 2s band, which accommodates two electrons, followed by the so-called "p-band" (occupied by six electrons) which mainly originates from N 2p states but also contains a significant contribution from Zr 4d orbitals; the next bands are primarily derived from Zr 4d states and, thus, are denoted as "d band" which—in the case of ZrN—overlaps with the "p band." Between the "p band" and "d band" there is a similar minimum in the DOS at eight valence electrons as in TiC. From this minimum the DOS steadily increases till all nine valence electrons of ZrN are accommodated, so that  $E_F$  lies in the "d band" with a relatively high DOS. This is one of the reasons that ZrN is a superconductor.

Several experiments have been interpreted on the basis of these band-structure results,<sup>4</sup> for example x-ray emission spectra,<sup>4</sup> angle-resolved-photoemission results,<sup>14</sup> or optical properties.<sup>15</sup> In general, the agreement between theory and experiment is rather good, so that the band structure of ZrN in the NaCl structure is well established.

### III. DUAL ION-BEAM SPUTTER DEPOSITION OF NITRIDES

By using the technique of dual ion-beam sputtering<sup>16</sup> Johansson *et al.* have examined the experimental conditions for the deposition of thin nitride films.<sup>17</sup> With the target metal  $M = \text{Hf, Zr, and Ti}$  and different ion sources (e.g., in terms of operating energy or nitrogen dilution by Ar or Ne) the  $[\text{N}]/[\text{M}]$  ratio could be varied over a wide range. A first stable phase is found for an  $[\text{N}]/[\text{M}]$  ratio of unity, the well-known golden-colored, metallic mononitrides. In the case of Hf-N (Ref. 18) and Zr-N (but not for Ti-N) another stable "higher-[N]-nitride" at composition  $[\text{N}]/[\text{M}] = 1.33$  is found. This phase is insulating, transparent, and according to very recent x-ray-diffraction experiments<sup>19</sup> it is closely related to the B1 (NaCl) structure of the mononitrides, but it shows a small rhombohedral distortion. Small inert-gas atoms, such as, Ne (to some extent also Ar) are incorporated in the higher-[N] nitride<sup>18</sup> reaching a  $[\text{Ne}]/[\text{Hf}]$  ratio of 0.25 at a composition of  $[\text{N}]/[\text{Hf}] = 1.33$ . Combining these observations<sup>17-19</sup> we propose for this insulating phase a metal-vacancy structure  $M_3N_4$  which is derived from the B1 structure by leaving 25% of the metal sites vacant. The insulator  $Zr_3N_4$  was reported,<sup>20</sup> but it was not well characterized.

### IV. ELECTRONIC STRUCTURE OF $Zr_3N_4$

Since the experimentally observed composition of the insulating zirconium nitride is close to the ratio 3/4 for  $[\text{Zr}]/[\text{N}]$ , we will denote it as  $Zr_3N_4$ . The structure is not known in detail, but should be closely related to NaCl. For NbO there exists an ordered defect structure with 25% vacancies on both the metal and nonmetal sublattices. The electronic structure of NbO has been investigated recently.<sup>21,22</sup> For  $Zr_3N_4$  we suggest a structure analogous to NbO which can be described as a NaCl

structure (containing four formula units) with one of the four Zr atoms removed (void,  $\square$ ), but all four N atoms remaining as shown in Fig. 1. The defect structure can be denoted as  $\square Zr_3N_4$  indicating that the one nitrogen (at the corner of Fig. 1) is crystallographically inequivalent from the three others which surround the void. Recently this structure has also been used to represent the metal defects of scandium sulfide<sup>23</sup> assuming  $\text{Sc}_3\text{S}_4$  or the nonmetal defects of titanium carbide<sup>9</sup> with  $\text{Ti}_4\text{C}_3$ .

The total number of valence electrons in  $Zr_3N_4$  is 32 ( $3 \times 4$  from Zr plus  $4 \times 5$  from N). Since the s and p bands of the four nitrogen atoms can accommodate ( $4 \times 8$ ) just 32 electrons, this octet argument could possibly account for the insulating nature of this defect structure.

In order to investigate the electronic properties of this suggested structure, energy-band calculations by the augmented-spherical-wave method<sup>24</sup> have been done for  $Zr_3N_4$  and the corresponding Ti and Hf compounds, assuming the defect structure above (Fig. 1). In these nonrelativistic ASW calculations the atomic sphere approximation (ASA) is used and exchange and correlation effects are treated by the local-density approximation.

For the three nitrides  $\text{Ti}_3\text{N}_4$ ,  $\text{Zr}_3\text{N}_4$ , and  $\text{Hf}_3\text{N}_4$  self-consistent ASW calculations yield the DOS as shown in Fig. 2 which are rather similar for all three compounds. The last one with the heavy element Hf should be done relativistically, but the nonrelativistic results are included for completeness. Starting with the ZrN results (corresponding to the NaCl structure), we find that the Fermi energy is significantly lowered from the d band to the minimum in the DOS between the p and d bands, indicating high stability. Therefore this defect structure is nearly an insulator. In all three cases, however, there remains some overlap between the p and d bands, so that the present results indicate the systems to be metallic. Exper-

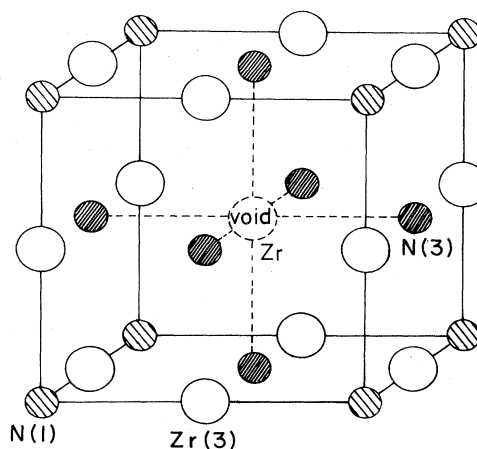


FIG. 1. Proposed crystal structure for  $Zr_3N_4$ . In terms of the NaCl structure the center Zr atom has been removed and this void is octahedrally surrounded by six N atoms; the remaining Zr (open circle) and the other nitrogen  $N_1$  (1 site) (at the corner) keep their first shell coordination six as in the NaCl structure;  $N_3$  (3 sites) is surrounded by four Zr atoms and two Zr voids.

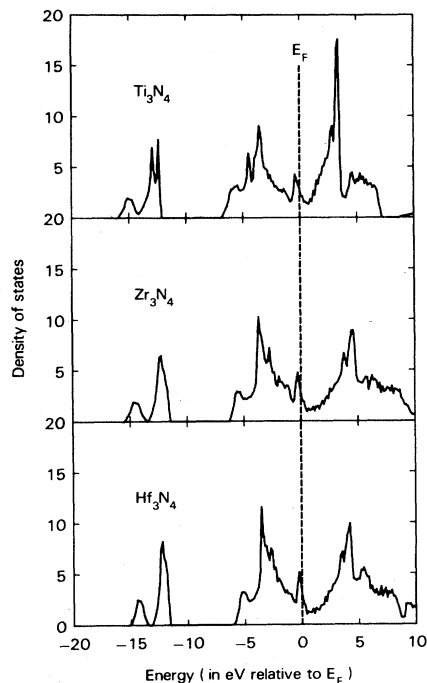


FIG. 2. Densities of states (in states per eV per formula unit) obtained by ASW calculations assuming the crystal structure of Fig. 1. Energy (in eV) is with respect to the Fermi energy  $E_F$ .

imentally, however, only the Ti compound remained metallic, while the other two were found to be insulators.

There are three possible reasons why the present calculations do not account for the insulating nature of the "higher-[N] nitride."

(i) The real crystal may differ significantly from the assumed ordered defect structure of  $Zr_3N_4$ .

(ii) The atomic sphere approximation commonly used in the ASW calculations could be less reliable in a system with vacancies (empty spheres) than in metallic systems.

(iii) The local-density approximation for treating exchange and correlation generally tends to give too small a gap in insulators and could, in the present case, be responsible for the  $Np-Zrd$  separation which is too small to yield a gap.

The chemical bonding of this defect structure is of particular interest. It can be better understood by decomposing the total DOS (Fig. 2) into site and  $l$ -projected components which can be derived within the ASW formalism.<sup>23</sup> In the vicinity of each atom, the wave function is expanded in spherical harmonics making possible a decomposition of the charge in each state according to site and angular momentum. Such a decomposition is shown in Fig. 3 for  $Zr_3N_4$  and allows the following observations: the two types of nitrogen sites differ significantly in their DOS, the one corresponding to N(1 site) which is octahedrally surrounded by six Zr atoms lies about 3 eV below that of N(3 sites) which has four Zr atoms and two voids in its first coordination shell. This downward shift is

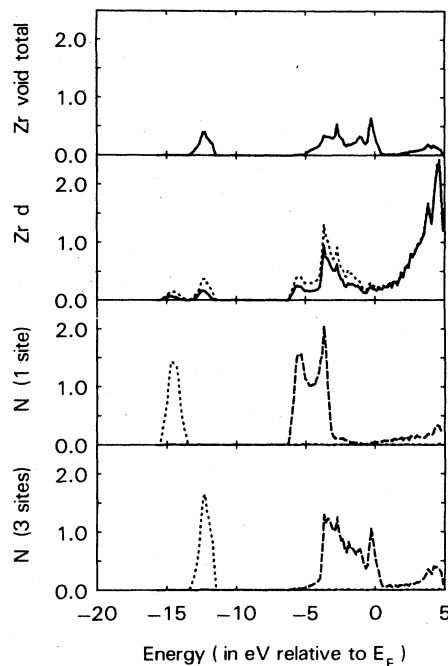


FIG. 3. Site and  $l$ -projected DOS of  $Zr_3N_4$ : (a) Zr void, (b) Zr  $d$  (solid line) and Zr total (dotted line), (c) N (1 site) coordinated by six Zr atoms;  $s$  (dotted line) and  $p$  (dashed line), and (d) N (3 sites) face centered in Fig. 1 coordinated by four Zr atoms; as  $c$ ).

mainly caused by an electrostatic interaction (different charge transfer and Madelung stabilization), but originates partly from a change in covalent interactions with four or six nearest neighbors. The relatively strong interaction between N and Zr can be seen from the Zr DOS which is high, especially for N(1 site) in the region of the N  $p$  bands. It is interesting to note that the DOS of the Zr void is rather large and looks similar in shape to that of N(3 sites). In particular, the peak just below  $E_F$  appears in the N(3 sites) and the Zr void DOS, but not in the Zr DOS itself, although both of these spheres are first nearest neighbors to N(3 sites) (see Fig. 1). This observation suggests that this peak corresponds to N  $2p$  dangling bonds or nonbonding states whose wave functions tail mainly into the Zr void where they are expanded in partial waves leading to the relatively high Zr void DOS. The other N  $2p$  states interact with the orbitals of the four Zr nearest neighbors and lead to the lower part of the N(3 sites) DOS in the  $p$  band. This mechanism explains the broader  $p$ -band width of the N(3 sites) in comparison to the N(1 site) DOS, an effect opposite to what one would expect from the simple argument of coordination numbers (four and six, respectively).

This difference between the two types of nitrogen suggests another possibility for the occurrence of an insulating phase: the real insulating zirconium nitride (ordered or disordered) could have nitrogen sites which are coordinated by five rather than four or six Zr atoms as assumed in the present  $Zr_3N_4$  structure.

## V. MATERIAL FOR A JOSEPHSON-JUNCTION DEVICE

The importance of this insulating phase stems from the fact that in combination with the superconductor ZrN it creates the possibility of building a common-lattice Josephson-junction device<sup>25</sup> with ZrN/Zr<sub>3</sub>N<sub>4</sub>/ZrN. In this case the superconductor and the insulator have essentially the same crystal structure (besides the defects) and the same constituent elements, i.e., it is isostructural and isochemical. This is not the case in the usual materials for Josephson junctions where lead alloys or Nb are used for the superconductors separated by insulating oxides, so that tension at the interface could occur.

In the case of ZrN there is an even better chance to minimize the lattice mismatch at the interface. For that purpose total energy calculations of the relevant systems have been performed and they are summarized in Fig. 4. A comparison of the equilibrium lattice constants between ZrN in the NaCl structure [Fig. 4(c)] and the defect case [Fig. 4(d)] shows only a mismatch of about 1.5%.

In order to improve on this situation, an attempt has been made to implant inert gases into the void of Zr<sub>3</sub>N<sub>4</sub>. This should not significantly alter the electronic structure, i.e., the insulating character should remain, but it should affect the lattice constant. Therefore, ASW calculations were done to study the effects of inert-gas implantation by replacing the Zr void by Ne or Ar. It can be seen that for Ne [Fig. 4(b)] an almost perfect match with ZrN(NaCl) is

achieved, while Ar [Fig. 4(a)] would cause a significant increase in the lattice constant.

The site and *l*-projected DOS of Ne in NeZr<sub>3</sub>N<sub>4</sub> (Fig. 5) show that, except for the additional Ne 2*p* DOS, the features are similar to the Zr void DOS [Fig. 3(a)]. Therefore, the DOS corresponding to Ne (or Zr void) do not indicate interactions, but should be interpreted to originate mainly from the tails of the surrounding nitrogen wave functions.

Experimentally it was found that about 10 at. % Ne can be implanted without destroying the insulating nature, but only about 4 at. % Ar could be incorporated. This observation is in good agreement with the theoretical prediction and supports the assumed defect structure of Fig. 1, since a complete filling of the Zr void corresponds to 12.5 at. %. The smaller Ne atom occupies about 80% of all the voids while the large Ar atom can only reach about 30% void occupancy.

Recent calculations<sup>26</sup> predicted modifications in the direct and indirect gaps of the tetrahedral semiconductors such as GaAs when He atoms are placed at interstitial sites. This is another example for inert-gas atoms affecting solid-state properties.

From these results it appears that the combination ZrN in the NaCl structure and NeZr<sub>3</sub>N<sub>4</sub> should be ideal in terms of the interface for a Josephson-junction device. The implanted Ne plays a double role. On the one hand, it works as a spacer to find the perfect lattice match and on the other hand, it could stabilize the defect structure in

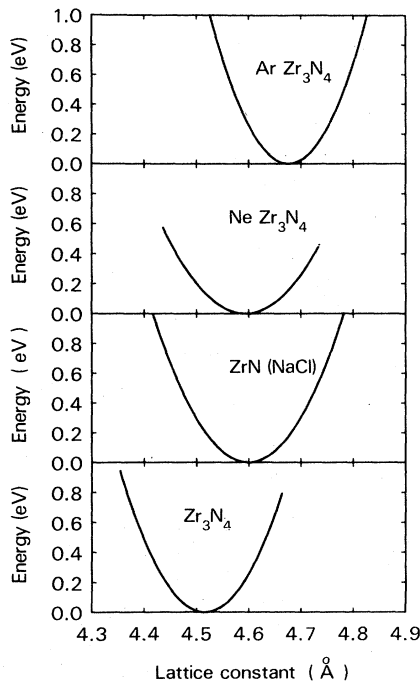


FIG. 4. Total energy (with respect to its minimum) as a function of lattice constant obtained by ASW calculations. The void in Zr<sub>3</sub>N<sub>4</sub> (Fig. 1) is substituted by Ar, Ne, and Zr, respectively, leading to the results (a)–(c), where (c) is the NaCl structure; (d) corresponds to Zr<sub>3</sub>N<sub>4</sub>.

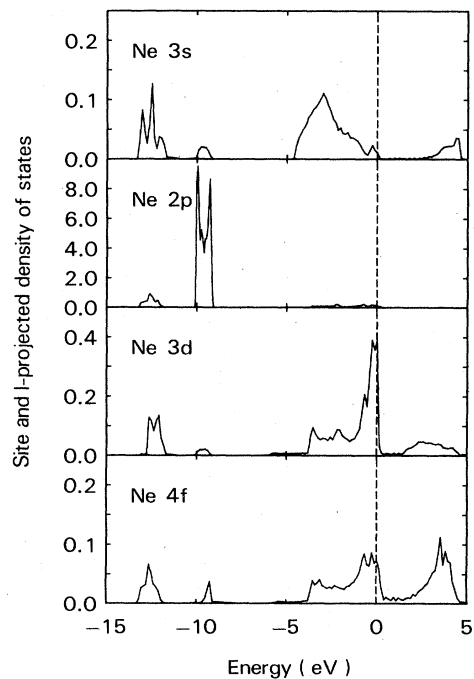


FIG. 5. Site and *l*-projected density of states (in states per eV per Ne atom) for Ne in NeZr<sub>3</sub>N<sub>4</sub>. Energy (eV) is with respect to the Fermi energy  $E_F$ .

the sense that diffusion from the superconducting into the insulating defect structure is prevented. Consequently from a materials point of view it looks like an interesting alternative for building Josephson-junction devices.

#### ACKNOWLEDGMENT

This work was partly supported by the Hochschuljubiläumsstiftung der Stadt Wien.

\*Permanent address: Institut für Technische Elektrochemie, Technische Universität Wien, A-1060 Vienna, Austria.

†Permanent address: Linköping Institute of Technology, S-581 83, Linköping, Sweden.

<sup>1</sup>J. L. Calais, *Adv. Phys.* **26**, 847 (1977).

<sup>2</sup>A. Neckel, P. Rastl, R. Eibler, P. Weinberger, and K. Schwarz, *J. Phys. C* **9**, 579 (1976).

<sup>3</sup>K. Schwarz, *J. Phys. C* **10**, 195 (1977).

<sup>4</sup>K. Schwarz, H. Ripplinger, and A. Neckel, *Z. Phys. B* **48**, 79 (1982).

<sup>5</sup>P. Blaha and K. Schwarz, *Intern. J. Quantum Chem.* **23**, 1535 (1983).

<sup>6</sup>A. Neckel, *Intern. J. Quantum Chem.* **23**, 1317 (1983).

<sup>7</sup>K. Schwarz and N. Rösch, *J. Phys. C* **8**, L433 (1975).

<sup>8</sup>G. Ries and H. Winter, *J. Phys. F* **10**, 1 (1980).

<sup>9</sup>J. Redinger, R. Eibler, P. Herzig, A. Neckel, R. Podloucky, and E. Wimmer, *J. Phys. Chem. Solids* **46**, 383 (1985).

<sup>10</sup>D. A. Papaconstantopoulos and W. E. Pickett, *Phys. Rev. B* **31**, 7093 (1985).

<sup>11</sup>L. Porte, *Solid State Commun.* **50**, 303 (1984).

<sup>12</sup>A. Dunand, H. D. Flack, and K. Yvon, *Phys. Rev. B* **31**, 2299 (1985).

<sup>13</sup>P. Blaha, J. Redinger, and K. Schwarz, *Phys. Rev. B* **31**, 2316 (1985).

<sup>14</sup>A. Callenäs, L. I. Johansson, A. N. Christensen, K. Schwarz,

P. Blaha, and J. Redinger, *Phys. Rev. B* **30**, 635 (1984).

<sup>15</sup>R. Eibler, M. Dorrer, and A. Neckel, *J. Phys. C* **16**, 3137 (1983).

<sup>16</sup>J. M. E. Harper, J. J. Cuomo, and H. T. G. Hentzell, *Appl. Phys. Lett.* **43**, 547 (1983).

<sup>17</sup>B. O. Johansson, H. T. G. Hentzel, J. M. E. Harper, and J. J. Cuomo (unpublished).

<sup>18</sup>B. O. Johansson, J.-E. Sundgren, U. Helmersson, and M. K. Hibbs, *Appl. Phys. Lett.* **44**, 670 (1984).

<sup>19</sup>B. O. Johansson (unpublished).

<sup>20</sup>R. Juza, A. Rabenau, and I. Nitschke, *Z. Anorg. Allg. Chem.* **332**, 1 (1964).

<sup>21</sup>E. Wimmer, K. Schwarz, R. Podloucky, P. Herzig, and A. Neckel, *J. Phys. Chem. Solids* **43**, 439 (1982).

<sup>22</sup>K. Schwarz, in *Basic Properties of Binary Oxides*, edited by A. Dominguez Rodriguez, J. Casting, and R. Marquez (Publicaciones de la Universidad de Sevilla, 1984), p. 43.

<sup>23</sup>D. K. Misemer and J. F. Nakahara, *J. Chem. Phys.* **80**, 1964 (1984).

<sup>24</sup>A. R. Williams, J. Kübler, and C. D. Gelatt, Jr., *Phys. Rev. B* **19**, 6094 (1979).

<sup>25</sup>K. Schwarz, A. R. Williams, J. J. Cuomo, J. H. E. Harper, and H. T. G. Hentzell, *Bull. Am. Phys. Soc.* **29**, 301 (1984).

<sup>26</sup>H. W. A. M. Rompa, M. F. H. Schuurmans, and F. Williams, *Phys. Rev. Lett.* **52**, 675 (1984).