[a]Permanent address: Institute of Materials Research, McMaster University, Hamilton, Ontario L8S 4M1, Canada.

[1]K. H. Michel and J. Naudts, Phys. Rev. Lett. 39, 212 (1977), and J. Chem. Phys. 67, 547 (1977).

[2]D. L. Price, J. M. Rowe, J. J. Rush, E. Prince, D. G. Hinks, and S. Susman, J. Chem. Phys. 56, 3697 (1972); J. M. Rowe, D. G. Hinks, D. L. Price, S. Susman, and J. J. Rush, J. Chem. Phys. 58, 2039 (1973).

[3]H. J. Verweel and J. M. Bijvoet, Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem. 100, 201 (1938); J. M. Bijvoet and J. A. Lely, Recl. Trav. Chim. Pays Bas 59, 908 (1940).

[4]J. M. Rowe, J. J. Rush, and E. Prince, J. Chem. Phys. 66, 5147 (1977); Y. Kondo, D. Schoemaker, and F. Lüty, Phys. Rev. B 19, 4210 (1979).

[5]K. D. Ehrhardt, thesis, University of Saarbrucken, 1981 (unpublished); K. D. Ehrhardt, W. Press, J. Lefebvre, and S. Haussühl, Solid State Commun. 34, 591 (1980).

[6]D. Fontaine, R. M. Pick, and M. Yvinec, Solid State Commun. 21, 1095 (1977); D. Fontaine and R. M. Pick, J. Phys. (Paris) 40, 1105 (1979).

[7]W. R. Fehlner and S. H. Vosko, Can. J. Phys. 54, 2159 (1976); R. S. Seymour and A. W. Pryor, Acta Crystallogr. Sect. B: 26, 1487 (1970).

[8]R. E. Wasylishen, B. A. Pettitt, and K. R. Jeffrey, to be published.

[9]S. Haussühl, Solid State Commun. 13, 147 (1973); W. Krasser, U. Buchenau, and S. Haussühl, Solid State Commun. 18, 287 (1976); S. Haussühl, J. Eckstein, K. Recker, and F. Wallrafen, Acta Crystallogr. Sect. A: 33, 847 (1977); M. Boissier, R. Vacher, D. Fontaine, and R. M. Pick, J. Phys. (Paris) 41, 1937 (1980); S. Haussühl, Solid State Commun. 32, 181 (1979); W. Krasser, B. Janik, K. D. Ehrhardt, and S. Haussühl, Solid State Commun. 30, 33 (1979).

[10]J. M. Rowe, J. J. Rush, N. Vagelatos, D. L. Price, D. G. Hinks, and S. Susman, J. Chem. Phys. 62, 4551 (1975); J. M. Rowe, J. J. Rush, E. Prince, and N. J. Chesser, Ferroelectrics 16, 107 (1977).

[11]J. M. Rowe, J. J. Rush, N. J. Chesser, K. H. Michel, and J. Naudts, Phys. Rev. Lett. 40, 455 (1978); K. H. Michel and J. Naudts, J. Chem. Phys. 68, 216 (1978); D. DeRaedt and K. H. Michel, Discuss. Faraday Soc. 69, 88 (1980).

[12]We have found in self-consistent-field calculations on $(CN)^-$ ions in an octahedral cage of positive charges that, with respect to the free ion, orientation along ⟨100⟩ results in an increase and orientation along ⟨110⟩ or ⟨111⟩ to a decrease in the dipole and quadrupole moments.

[13]M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids 25, 45 (1964); F. L. Hirshfeld and K. Mirsky, Acta Crystallogr. Sect. A: 35, 366 (1979).

[14]J. E. Gready, G. B. Bacskay, and N. S. Hush, Chem. Phys. 31, 467 (1978).

[15]P. C. Schmidt, A. Weiss, and T. P. Das, Phys. Rev. B 19, 5525 (1979); C. Muhlhausen and R. G. Gordon, Phys. Rev. B 23, 900 (1981).

[16]H. Tex, M. Müllner, R. Knoth, and A. Loidl, Solid State Commun. 36, 713 (1980).

Commensurate-Incommensurate Transitions in Two Dimensions: Discrete Models and Square Symmetric Substrates

H. J. Schulz

I. Institut für Theoretische Physik, Universität Hamburg, D-2000 Hamburg 36, West Germany

(Received 17 September 1980)

The phase diagram and the critical behavior of a discrete two-dimensional model of the commensurate-incommensurate transition is determined with use of an approximate mapping onto the six-vertex model. For an uniaxial substrate the critical behavior is that of the continuum case. For a square substrate either a single first-order transition or a second-order transition followed by a first-order transition is found.

PACS numbers: 64.60.Fr, 64.70.Kb

In adsorbed gas monolayers phase transitions between commensurate (C) and incommensurate (IC) structures have been observed,[1-6] both of first and second order. Current theories of these transitions are either restricted to $T=0$[7-9] or assume a substrate potential periodic only in one of two space directions,[9-11] and use a continuum approximation for the layer. Near the C-IC transition the IC state consists of large C regions separated by domain walls. The critical behavior of the transition is dominated by the walls. In the continuum models the walls can move freely; however, if the discrete nature of the layers is taken into account a periodic potential acts on the walls. At $T=0$ this leads to the appearance of infinitely many C phases, the so-called devil's staircase.[12] In this paper discrete models of the C-IC transition at $T\neq 0$ are treated

© 1981 The American Physical Society

for both uniaxial and square symmetric substrates. We shall always assume to be at sufficiently low-temperatures so that there are no free dislocations, i.e., the IC state is a "floating solid."[13]

We consider a square lattice (lattice constant a) of harmonically interacting atoms in a periodic potential of wavelength λ. Its energy is

$$U=U_0+W,\quad W=V\sum_{i,j}\cos\{2\pi[u_{ij}+v_{ij}+\delta(i+j)]\},$$

$$U_0=\sum_{i,j}\{A[(u_{i+1,j}-u_{ij})^2+(v_{i,j+1}-v_{ij})^2]+B[(u_{i,j+1}-u_{ij})^2+(v_{i+1,j}-v_{ij})^2] \tag{1}$$
$$+C(u_{i+1,j}-u_{i-1,j})(v_{i,j+1}-v_{i,j-1})\}.$$

Here i and j label the atoms with displacement components u_{ij} and v_{ij}, and $\delta=a/\lambda-1$. The minimum lines of W make a 45° angle with the x axis. We note that U_0 is not invariant under rotations (it is apparently impossible to construct an invariant expression bilinear in u_{ij}, v_{ij}), but this should not affect the C-IC transition.

To treat the statistical mechanics, following Villain,[14] we make the approximation

$$\exp[-\beta V\cos(2\pi u)]\approx K_0\sum_{n=-\infty}^{\infty}\exp[-\beta\mu(u-n)^2], \tag{2}$$

where μ is determined so that the first Fourier components in Eq. (2) agree, and the partition function follows as

$$Z=\sum_{\{n_{ij}\}}\int\prod_{i,j}du_{ij}dv_{ij}\exp\{-\beta[U_0+\mu\sum_{i,j}(u_{ij}+v_{ij}+\delta(i+j)-n_{ij})^2]\}, \tag{3}$$

where an *integer* variable n_{ij} is associated to each lattice point and a factor K_0^N has been omitted. The integrations over u_{ij}, v_{ij} can now be done, and only the sum over $\{n_{ij}\}$ remains, i.e., Z describes the statistical mechanics of a system with energy functional

$$H_n=\sum_{i,j,l,m}a_{lm}[n_{i+l,j+m}-n_{ij}-\delta(l+m)]^2; \tag{4a}$$

$$a_{lm}=\frac{\mu^2}{2N}\sum_q\frac{[(A+B)(Q_x^2+Q_y^2)-4CQ_x'Q_y']\exp[ia(lq_x+mq_y)]}{(AQ_x^2BQ_y^2+\mu)(AQ_y^2+BQ_x^2+\mu)-(2CQ_x'Q_y'+\mu)^2}, \tag{4b}$$

$$Q_\alpha=2\sin(\tfrac{1}{2}q_\alpha a),\quad Q_\alpha'=\sin q_\alpha a.$$

The a_{lm} decay exponentially for large l, m; the decay is the faster the larger V relative to the elastic energy (1b). The variables n_{ij} have a simple physical meaning: $n_{i+1,j}-n_{ij}=0,1$ means that the corresponding adjacent atoms are in adjacent wells or have one empty well between them, respectively. H_n is a generalized roughening model. For $\delta=0$ this model has a Kosterlitz-Thouless (KT)[15] transition at $T_0\approx 3.5a_{10}$.[16] The transformation $n_{ij}\to n_{ij}+\delta(i+j)$ shows that the same transition occurs for all integer values of δ.

To treat the general case $\delta\neq 0$ we make two approximations: (i) we retain only nearest and next-nearest interactions in H_n. For $T=0$ it is easy to see that this suppresses the devil's-staircase phenomenon inherent in the original model (1) and only a finite number of commensurate phases remains. However, due to the exponential decrease of a_{lm}, at $T\gtrsim 2a_{20}$ only low-order C phases are possible. Therefore, restricting ourselves to that temperature range, the truncation of H_n is well justified, though higher terms will change somewhat the form of the phase boundaries. (ii) We consider only $\delta\approx\frac{1}{2}$. In the partition sum then we allow only the two lowest-energy states of each nearest-neighbor bond, i.e., $n_{i+1,j}-n_{ij}=0,1$, etc. This restriction still allows the existence of C regions separated by walls, i.e., of the configurations which have been shown to determine the critical behavior of the C-IC transitions in the continuum models.[9-11] Therefore we do not expect the essential physics of the transition to be changed by this restriction. The six allowed configurations of the unit square of the lattice are shown in Fig. 1(a), where an arrow pointing right or upward means increase of n_{ij} by 1, whereas elsewhere the n_{ij} are constant.

We now turn each arrow by $\pi/2$, thus arriving at the configurations of Fig. 1(b), which are

those of the exactly solvable six-vertex model.[17,18] In the notations of Lieb and Wu[18] the energy parameters are

$$\epsilon_1 = 2(a_{11} - a_{-1,1}), \quad \epsilon_2 = 2a_{11}, \quad h = -v = (a_{10} + 2a_{11})(1 - 2\delta). \tag{5}$$

The phase diagram and critical behavior can be determined from the free energy per atom, obtained for small *fixed* $y = 2\langle n_{i+1,j} - n_{ij}\rangle - 1$ as[18,19]

$$F(y) = F(0) - 2vy - T[Z'|y| + \tfrac{1}{6}Z'''|y|^3] + O(y^4),$$
$$Z' = -2\Xi(\rho), \quad Z''' = 6[\pi/\Xi'(\rho)]^2\Xi''(\rho), \quad \rho = \tfrac{1}{2}(\lambda + \theta_0) \tag{6}$$

at $T < T_1\{\exp[(2\epsilon_2 - \epsilon_1)/T_1] - \cosh(\epsilon_1/T_1) = 1\}$, where the functions Ξ, λ, and θ_0 are given in terms of $\epsilon_{1,2}$ in Ref. 18. A similar expansion is valid near $y = \pm 1$.

In the thermodynamic limit only the value of y minimizing F contributes to the partition sum.[18] Thus the phase boundaries are given by $2v = \pm TZ'$ (Fig. 2). The 1/1, 2/3, and 1/2 C phases correspond to $y = -1, 0, 1$, respectively. Above T_c there is an IC (floating) solid phase. The transition at $\delta = \frac{1}{2}$, $T = T_1$ is of the KT type with an essential singularity of the free energy. Near $\delta = \frac{1}{2}$, T_c has a sharp spike of the form $T_1 - T_c \propto [\ln|\delta - \frac{1}{2}|]^{-2}$. Near $\delta = 0, 1$ our approximation (ii) becomes invalid. However, in analogy to $\delta = \frac{1}{2}$ we expect similar spikes of T_c, as drawn by dashed lines in Fig. 2. Furthermore, inclusion of more than next-nearest-neighbor couplings should cause higher-order C phases to appear between those of Fig. 2. For these phases a KT transition and a spike of $T_c(\delta)$ are expected at the corresponding rational values of δ.

Near the 2/3 phase the density of walls is $y/2$, near 1/1 and 1/2 it is $(1+y)/2$ and $(1-y)/2$, respectively. Near the phase boundaries the wall density is proportional to $|\delta - \delta_c(T)|^{1/2}$, the specific heat exponent is $\alpha = \frac{1}{2}$ on the IC side, and near T_1 the amplitude of this singularity vanishes like $(T_1 - T_c)^{-9/4}\exp[-\text{const}\,(T_1 - T_c)^{-1/2}]$, so that at $\delta = \frac{1}{2}$ only an essential singularity of the free energy is left. On the C side of the transition there are no critical divergences. These results are in complete agreement with those of the continuum model.[11] This equivalence may be understood if we note that in both cases in the IC phase there is a high number of possible low-energy states of the domain walls.

We now consider a square symmetric substrate, i.e.,

$$U = U_0 + W + V\sum_{i,j}\cos\{2\pi[u_{ij} - v_{ij} + \delta(i-j)]\}. \tag{7}$$

The analysis is the same as above; however, because of the two periodic potentials, two sets of integers $\{n_{ij}\}$ and $\{m_{ij}\}$ must be introduced, and the energy functional is

$$H_{nm} = \sum_{i,j,l,m} a_{lm}\{[n_{i+l,j+m} - n_{ij} - \delta(l+m)]^2 + [m_{i+l,j-m} - m_{ij} - \delta(l+m)]^2\} + \sum_{i,j;l>m} c_{lm}(h_{ijlm} - h_{ijml});$$
$$h_{ijlm} = [n_{i+l,j+m} - n_{ij} - \delta(l+m)][m_{i+l,j+m} - m_{ij} - \delta(l-m)], \tag{8a}$$
$$a_{lm} = \frac{\mu^2}{2N}\sum_q \frac{[(A+B)(Q_x^2 + Q_y^2) - 4CQ_x'Q_y' + 4\mu]\exp[ia(lq_x + mq_y)]}{(AQ_x^2 + BQ_y^2 + 2\mu)(AQ_y^2 + BQ_x^2 + 2\mu) - 4(CQ_x'Q_y')^2}, \tag{8b}$$
$$c_{lm} = \frac{\mu^2}{N}\sum_q \frac{(A-B)(Q_y^2 - Q_x^2)\exp[ia(lq_x + mq_y)]}{(AQ_x^2 + BQ_y^2 + 2\mu)(AQ_y^2 + BQ_x^2 + 2\mu) - 4(CQ_x'Q_y')^2}. \tag{8c}$$

The c_{lm} term describes the interaction between the n_{ij} and the m_{ij} systems. To be consistent with approximation (i) we consider only the nearest-neighbor (c_{10}) coupling. As above, variables y_1 and y_2 are introduced for the n and m systems, which for small y_1, y_2 give the density of walls in the two space directions near the 2/3 phase. Expanding the partition sum *at fixed* y_i gives

$$Z = \exp[-\tfrac{1}{2}\beta c_{10}N(y_1 + 1 - 2\delta)(y_2 + 1 - 2\delta)]Z_n(y_1)Z_m(y_2)$$
$$\times[1 + \tfrac{1}{2}\beta^2 c_{10}^2\sum_{i,j,l,m}\langle(h_{ij10} - h_{ij01} - \langle h_{ij10} - h_{ij01}\rangle_{nm})(h_{lm10} - h_{lm01} - \langle h_{lm10} - h_{lm01}\rangle_{nm})\rangle_{nm} + \cdots]. \tag{9}$$

Here N is the number of atoms in the system, $Z_{n,m}$ are the partition sums of the n and m systems for $c_{lm} = 0$, $\langle\cdots\rangle_{nm}$ are the corresponding averages, and only second-order terms have been written out explicitly. The correlation functions in Eq. (9) cannot be calculated directly for the discrete system; however, at least the long-range behavior can be expected to be the same as in the continuum case,

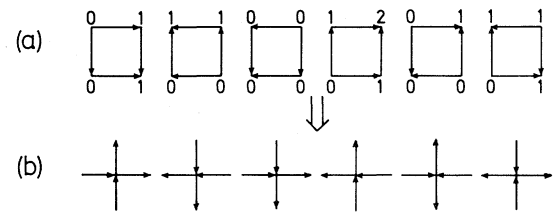

FIG. 1. The transformation from (a) H_n, integers show typical values of n_{ij} at the corners of the unit square in the shown configuration, to (b) the six-vertex model.

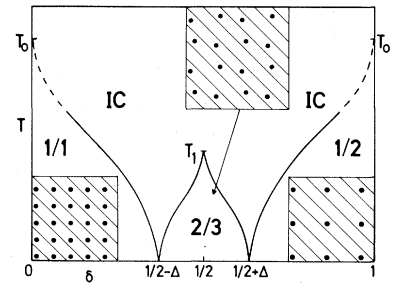

FIG. 2. The phase diagram in the δ-T plane $[\Delta = a_{11}/(2a_{10} + 4a_{11})]$. Insets show the atomic arrangements in the different C phases; straight lines indicate the maxima of the substrate potential.

for which an explicit calculation is possible.[11] These correlation functions have an algebraically decaying part which represents the domain walls of the IC phase and vanishes in the C phase ($y_1 = 0$ or $y_2 = 0$). Therefore the contribution to Z of this part has to vanish if $y_1 = 0$ *or* $y_2 = 0$. Especially, *no terms proportional to* y_i^2 *can appear*. A calculation that uses the continuum correlation functions shows that the second-order term can be expanded in powers of the y_i. The lowest-order term is proportional to $y_1 y_2$ and gives (for small c_{10}) only a small correction to the $y_1 y_2$ term in the free energy coming from the exponential prefactor in Eq. (9). In addition there is an exponentially decaying part coming from the C regions of the system. This part does not change nonanalytically through the C-IC transition, leading only to small corrections to the coefficients in $F(y_1, y_2)$. The form of the higher-order correlation functions implies that their contribution may also be expanded in powers of the y_i. Therefore, to lowest order in c_{10} we may neglect the square bracket in Eq. (9). The higher-order terms only change the coefficients of y_i in $F(y_1, y_2)$, *but no terms nonanalytic in* y_i *are introduced*. Thus the free energy is

$$F(y_1,y_2) = F(y_1) + F(y_2) + \tfrac{1}{2}c_{10}(y_1 + 1 - 2\delta)(y_2 + 1 - 2\delta), \tag{10}$$

where $F(y)$ is given by Eq. (6). Minimizing $F(y_1, y_2)$ shows that the C-IC transition may happen in two different ways: (i) For $c_{10} > 0$, i.e., repulsion between crossing walls, a second-order transition from the C to an uniaxial IC state ($y_1 = 0, y_2 \neq 0$ or $y_1 \neq 0, y_2 = 0$) occurs for $TZ' = |v|[2 + c_{10}/(2a_{10} + 4a_{11})]$. The critical behavior of this transition is the same as that in Eq. (6). At somewhat higher values of $|v|$ or T a *first-order* transition into an isotropic IC state ($y_1 = y_2$) occurs. (ii) For $c_{10} < 0$ (wall attraction) the C-IC transition is first order directly into the $y_1 = y_2$ state. In our model the sign of c_{10} is equal to the sign of $A - B$. Here only small values of y_i (2/3 state) have been considered; however, the same arguments apply near the other C states of Fig. 2. Thus, all the transition lines become either first order or are split into a second-order and a first-order line. The same two possibilities have been found by Bak *et al.*[7] in a $T = 0$ theory.

The author acknowledges helpful discussions with J. Friedel and T. Garel at Laboratoire de Physique des Solides, Université Paris–Sud, where most of this work was done.

[1]A. Thomy and X. Duval, J. Chim. Phys. 67, 1101 (1970).

[2]J. K. Kjems, L. Passell, H. Taub, J. G. Dash, and A. D. Novaco, Phys. Rev. B 13, 1446 (1976).

[3]M. D. Chinn and S. C. Fain, Phys. Rev. Lett. 39, 146 (1977).

[4]M. Nielsen, J. P. Mctague, and W. Ellenson, J. Phys. (Paris), Colloq. 38, C4-10 (1977).

[5]P. W. Stephens, P. Heiney, R. J. Birgeneau, and P. M. Horn, Phys. Rev. Lett. 43, 47 (1979); D. M. Butler, J. A. Litzinger, and G. A. Stewart, Phys. Rev. Lett. 44, 466 (1980).

[6]P. Vora, S. K. Sinha, and R. K. Crawford, Phys. Rev. Lett. 43, 704 (1979).

[7]P. Bak, D. Mukamel, J. Villain, and K. Wentowska, Phys. Rev. B 19, 1610 (1979).

[8]H. Shiba, J. Phys. Soc. Jpn. 46, 1852 (1979), and 48, 211 (1980).

[9]J. Villain, in *Ordering in Strongly Fluctuating Condensed Matter Systems*, edited by T. Riste (Plenum, New York, 1980), p. 221, and J. Phys. (Paris), Lett. 41, L267 (1980), and Surf. Sci. 97, 219 (1980).

[10]V. L. Pokrovsky and A. L. Talapov, Phys. Rev. Lett. 42, 65 (1979), and Zh. Eksp. Teor. Fiz. 78, 269 (1980) [Sov. Phys. JETP 51, 134 (1980)].

[11]H. J. Schulz, Phys. Rev. B 22, 5274 (1980).

[12]S. Aubry, in *Solitons in Condensed Matter Physics*, edited by A. R. Bishop and T. Schneider (Springer, Berlin, 1978), p. 264.
[13]D. R. Nelson and B. I. Halperin, Phys. Rev. B 19, 2457 (1979).
[14]J. Villain, J. Phys. (Paris) 36, 581 (1975).
[15]J. M. Kosterlitz and D. J. Thouless, J. Phys. C 6, 1181 (1973).
[16]S. T. Chui and J. D. Weeks, Phys. Rev. B 14, 4978 (1976).
[17]C. P. Yang, Phys. Rev. Lett. 19, 586 (1967); B. Sutherland, C. N. Yang, and C. P. Yang, Phys. Rev. Lett. 19, 588 (1967).
[18]E. H. Lieb and F. Y. Wu, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London, 1972), Vol. 1, p. 332. See glossary of this article (p. 486) for definition of the functions used in Eq. (6).
[19]In Ref. 18, z' and z''' are calculated only for $h = 0$. However, the coefficients given in Eq. (6) are obtained by a straightforward generalization of that calculation to the case $h = -v$.

Direct Evidence for Intrinsically Broken Chemical Ordering in Melt-Quenched Glasses

W. J. Bresser, P. Boolchand, and P. Suranyi
Physics Department, University of Cincinnati, Cincinnati, Ohio 45221

and

J. P. de Neufville
Energy Conversion Devices, Troy, Michigan 48084
(Received 8 January 1981)

The chalcogen site in bulk glasses of $GeSe_2$ and GeS_2 has been probed via nuclear quadrupole interactions with use of $^{129}Te^m$ impurity atoms as parent in ^{129}I Mössbauer emission spectroscopy. Two distinct types of chalcogen sites are observed and are shown to provide direct evidence for intrinsically broken chemical ordering in these network glasses. The composition dependence of the site parameters in pseudobinary-alloy glasses indicates the presence of characteristic large clusters rather than a continuous random network.

PACS numbers: 61.16.-d, 61.40.Df, 76.80.+y

Nuclear quadrupole resonance (NQR) experiments have recently provided detailed information on the atomic structure of alloy network[1] and metallic[2] glasses. The average electric field gradient (EFG) eV_{zz} and particularly the asymmetry parameter $\eta = |(V_{xx} - V_{yy})/V_{zz}|$ of the EFG tensor contain information characteristic of the atomic environment which can be interpreted quantitatively in terms of the same parameters in elemental solids. However, the application of NQR to chalcogenide glasses is restricted because there are no stable Se or Te isotopes that have a nonzero nuclear quadrupole moment eQ in the ground state. In this Letter we show that by means of a novel technique, ^{129}I Mössbauer emission spectroscopy, very precise nuclear quadrupole interaction (NQI) data are obtainable on chalcogen sites in these covalent glasses.

The basic idea of this technique is to measure the EFG, η, and electron charge density via the NQI of daughter ^{129}I nuclei at chalcogen sites by doping pseudobinary alloys such as g-$GeSe_{2-x}Te_x$ and g-$GeS_{2-x}Te_x$ with parent $^{129}Te^m$ atoms. The details of this technique and its application to elemental chalcogen glasses have been given previously.[3] Purified elements were sealed in evacuated quartz ampules in stoichiometric ratios and alloyed at 900 °C for 24 h before quenching in cold water. The glass transitions (T_g) of the g-$GeSe_{2-x}$-Te_x alloys were studied by differential scanning calorimetry. The T_g results were in quantitative agreement with the work of Sarrach, de Neufville, and Haworth,[4] which indicated the absence of phase separation in this alloy system. Figure 1 shows some of the Mössbauer spectra obtained.

The central discovery of the present work is that in bulk melt-quenched alloy glasses of $GeSe_{2-x}Te_x$ and $GeS_{2-x}Te_x$ even as $x \to 0$ there are two inequivalent I sites A and B. For example, as can be seen in Fig. 1, a qualitative improvement in the fit to a g-GeS_2 spectrum results in going from a one-site to a two-site fit. The NQI parameters $e^2QV_{zz}^A$, $e^2QV_{zz}^B$, η^B, and η^A for $GeSe_{2-x}Te_x$ alloys are shown as a function of x in

© 1981 The American Physical Society