

Chamberlin, Mozurkewich, and Orbach Respond.

R. V. CHAMBERLIN, GEORGE MOZURKEWICH, and
R. ORBACH [Phys. Rev. Lett. 53, 1025 (1984)].

Editorial error caused an out-of-date version of the text to be published. The version which should have appeared is as follows:

Chamberlin, Mozurkewich, and Orbach Respond.

In a recent Letter¹ we reported that the time decay of the thermoremanent magnetization in spin-glasses is accurately characterized by a stretched exponential of the form $\sigma_{\text{TRM}}(t) \propto \exp[-(t/\tau_p)^{1-n}]$. Furthermore, we showed that the effective relaxation time (τ_p) can be written in terms of the time-stretch exponent (n) and two temperature-independent constants C and ω :

$$\tau_p^{1-n} = (1-n)/C\omega^{1-n}. \quad (1)$$

Ngai and Rajagopal² are correct when they say that in order to relate this empirical form for τ_p to that predicted by the Ngai model,

$$\tau_p^{1-n} = (1-n)\tau_0(e^\gamma\omega_c)^n, \quad (2)$$

we made an assumption, namely that $\omega_c = 1/\tau_0 \propto \omega$. Indeed, as they have demonstrated, τ_0 can be chosen so that $t \gg \tau_0$, which then satisfies the limit used by Ngai in deriving Eq. (2). Hence, our statement that "... (the Ngai) theory in its present form is (not) directly applicable to spin-glasses" was an unfounded conclusion, for which we apologize.

The ambiguity arises because experimentally we

measure τ_p and n , so that only the product $C\omega^{1-n} = 1/\tau_0(e^\gamma\omega_c)^n$ is uniquely determined. Thus, there is complete freedom in choosing one of the variables (say τ_0) provided the other variable (ω_c) is given the necessary temperature dependence to fit the data. Our choice for τ_p [Eq. (1)] was motivated solely by the empirical fact that it is the only choice that makes both ω_c and τ_0 constant throughout the spin-glass regime; i.e., it is the only choice in which the entire temperature dependence of τ_p is contained in the unambiguously extracted temperature dependence of n . An independent measurement of τ_0 or ω_c is necessary before the correct choice for τ_p can be unequivocally established.

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¹R. V. Chamberlin, George Mozurkewich, and R. Orbach, Phys. Rev. Lett. 52, 867 (1984).

²K. L. Ngai and A. K. Rajagopal, preceding Comment [Phys. Rev. Lett. 53, 1024 (1984)].

New Model for the Alloy (GaAs)_{1-x}Ge_{2x}.

H. HOLLOWAY and L. C. DAVIS [Phys. Rev. Lett. 53, 830 (1984)].

Through a production error, the contents of printed pages 831 and 832 have appeared in reverse order. In addition, explanatory material was inadvertently omitted from Fig. 3. The entire Letter is reprinted herewith on the following pages.

New Model for the Alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$

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We show that a previous model for $(\text{GaAs})_{1-x}\text{Ge}_{2x}$, when more accurately analyzed, does not fit the observed composition dependence of the direct energy gap. A simple model for the lattice disorder is proposed. This model fits the composition dependence of the gap with no adjustable parameters. Our results show that antisite disorder and the transition from zinc-blende to diamond symmetry have no significant influence on the energy gap of this material.

PACS numbers: 64.60.Cn, 61.55.Hg, 71.25.Tn

Metastable $(\text{GaAs})_{1-x}\text{Ge}_{2x}$, covering the entire composition range, has been prepared both by pyrolytic reactions¹ and by sputtering.² This alloy has attracted attention because its energy-gap versus composition curve exhibits unusually pronounced bowing. It has also been noted³⁻⁵ that, since the components have different symmetries, the alloy must show a transition with composition from the zinc-blende to the diamond structure. D'yakonov and Raikh³ (DR) have considered $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ in terms of percolation on a diamond lattice and have suggested that infinite clusters of GaAs cease to exist for $x \geq 0.6$. Consequently a diamond phase with complete antisite disorder of the GaAs component could occur by random formation of separate site and antisite clusters of GaAs, without energetically unfavorable Ga-Ga and As-As nearest-neighbor (NN) pairs. In contrast, Newman and Dow⁵ (ND) have postulated an order-disorder transition that arises from a local minimum in the free energy. In this case it was assumed that the atoms can rearrange cooperatively to optimize NN interactions. This model was used to interpret the composition dependence of the energy gap, with the critical composition for the order-disorder transformation being an arbitrary parameter. Both of these explanations attributed discontinuities in the slope of the energy-gap versus composition curve to the order-disorder transition, but the two models involve quite different values for the critical Ge concentration at which a discontinuity occurs ($x = 0.6$ in DR and $x = 0.3$ in ND). Inspection of the published data (Fig. 3) suggests that the existence of discontinuities is not well established; the data are consistent with a smooth, though deeply bowed, curve.

In this Letter we demonstrate three things. First, that the ND model, when more accurately analyzed, does not fit the observed energy gap. The model was tested previously using the virtual-crystal approximation (VCA), which breaks down

because of the strong disorder scattering here. This effect is accounted for fully in the present work. Second, we show that the observed composition dependence of the energy gap is in accord with a simple statistical model for the alloy lattice. *This model has no adjustable parameters.* Third, while our model agrees with DR in restricting antisite disorder to Ge-rich alloys, we show that this feature has almost no influence on the energy gap (in the absence of As-As NN). Nearly identical results are obtained in the absence of antisite disorder.

To obtain a more accurate energy gap for the alloy than that given by VCA, we use the Haydock recursion method.⁶ Accurate spectral weight functions, $A(k, E)$, can be calculated for a tight-binding model of the electronic structure.⁷ We assume that separations of peaks in $A(k, E)$ spectra determine the energy gap (and the optical absorption edge). Large clusters (typically of 1000–1600 atoms) with any atomic arrangement can be analyzed. We use the same tight-binding model as ND,^{5,8,9} the only additional parameter in our work being the position of the Ge valence-band maximum relative to GaAs. To ensure that a Ge impurity on a Ga site in GaAs does not have a deeply bound donor level, we chose the Ge valence band to be 1 eV higher. In the VCA this offset has no influence on the gap and in the recursion method it has negligible effect over a wide range of values (–1 to 2 eV).

In Fig. 1(a) we show the spectral weight functions for the Γ_1 and Γ_{15} points (in zinc-blende notation) for $x = 0.5$ with the atoms completely randomly arranged as specified by ND for this composition. The bottom of the conduction band is at Γ_1 and the top of the valence band is at Γ_{15} . Quite independently of the choice of offset we found that the two spectral weights overlap, implying that the energy gap vanishes. Considerable disorder scattering is evident. We also show the energies of the states that are predicted by VCA, which gives a gap of 0.7 eV in sharp contrast to the results for the ND

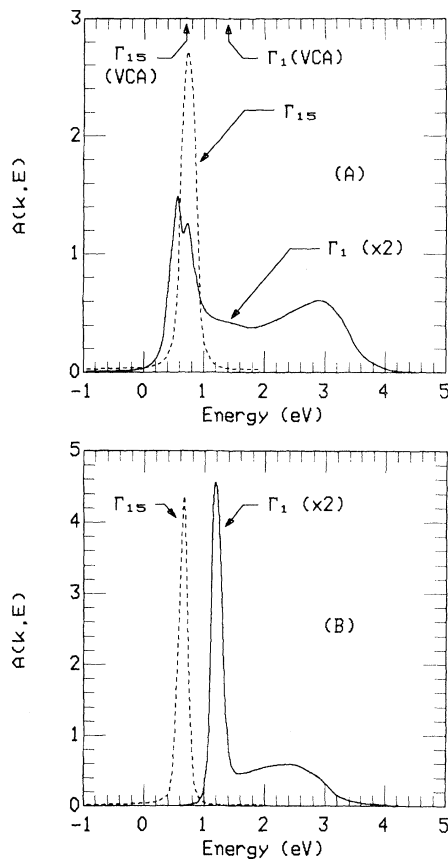


FIG. 1. Spectral weight functions for the Γ_1 (conduction-band) and Γ_{15} (valence-band) states in $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ when $x=0.5$. (Units on the ordinate are states/eV/spin/atom.) (a) With the lattice described by the ND model. (The splitting of the Γ_1 peak near 0.6 eV is an artifact.) The energies predicted by the generalized VCA of ND are also shown. (b) With the lattice described by the present model.

model with the more accurate recursion method.

In developing a model for $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ we found it necessary to make only two assumptions about NN, plus the assumption of randomness:

(1) *Ga and As atoms occur exclusively as Ga-As NN pairs.* (This differs from DR and ND.) With both the pyrolytic and sputtering growth methods the experimental conditions are such that As is present in excess over that required for complete reaction with Ga, but only enough As is incorporated to maintain stoichiometry. (The volatility of As at the substrate temperatures used precludes formation of a condensed As phase.) The only simple interpretation of this observation is that each Ga atom binds an NN As atom. Since at equilibrium the alloy would segregate into Ge and GaAs phases, we may expect that once Ga-As pairs are formed they will have negligible tendency to separate.

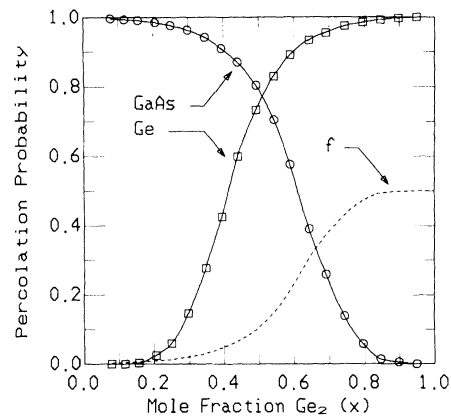


FIG. 2. Approximate percolation probabilities for the GaAs and Ge components of $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ with the lattice described by our model. The dashed curve shows the antisite fraction of the GaAs component.

(2) *Ga-Ga and As-As NN pairs do not occur to any significant extent.* (This differs from ND.) This is reasonable in the light of the small tendency for such energetically disfavored pairs to occur in GaAs. This assumption is equivalent to postulating that during growth the atoms at the surface are mobile with a range of at least one or two atom sites.

(3) *Subject to the preceding restrictions, the Ge atoms and Ga-As pairs are randomly arranged on a diamond lattice.*

With the postulates above the alloy lattice is fully specified. However, in order to discuss previous treatments we describe briefly its statistical properties. The system resembles a simply substituted diamond lattice, but with the modification that one of the components only occurs as atom pairs. Preliminary Monte Carlo analysis shows that the percolation probabilities do not differ greatly from those of simply substituted diamond.¹⁰ Figure 2 shows approximate percolation probabilities obtained from clusters of 512 atoms. (Infinite clusters would be expected to give a sharper transition from nonpercolation to percolation.) We also show the antisite fraction as a function of composition. Here the antisites arise from finite isolated GaAs clusters that have either complete site or complete antisite occupancy within each cluster. Thus the antisite fraction is $f = (1 - P)/2$, where P is the percolation probability for GaAs. We may distinguish three regions with different characteristics in the following approximate composition ranges:

(1) $0 < x < 0.25$. Here the GaAs component exists almost entirely in infinite connected clusters. The Ge component occurs as finite isolated clusters

of one or more atoms.

(2) $0.25 < x < 0.75$. With increasing x in this region the fraction of Ge atoms in infinite connected clusters increases from near zero to near unity. Simultaneously, the Ga-As pairs change from infinite connected clusters to finite isolated clusters. This marks the onset of antisite disorder. The percolation probability for Ga-As pairs decreases from near unity to near zero and correspondingly the antisite fraction increases to near 0.5.

(3) $0.75 < x < 1$. In this region almost all of the Ge component is in infinite clusters. The GaAs component is present as finite isolated clusters that are randomly oriented to give complete antisite disorder ($f=0.5$). The change in antisite disorder from the preceding region to this one corresponds to the transition between the zinc-blende and diamond symmetries.

For application of the recursion method, alloy clusters subject to the preceding NN restrictions were constructed by Monte Carlo methods. Since periodic boundaries were required,⁸ these clusters were subjected to the further constraint that the rules relating to Ga-As pairs and to Ga-Ga and As-As NN would be met across the boundaries of adjacent identical clusters. Most of the calculations were done with 41 recursions on clusters of 1024 atoms. Selected points were checked with 48 recursions on clusters of 1600 atoms, which gave essentially identical results.

The spectral weight functions for the new model when $x=0.5$ are shown in Fig. 1(b). It is immediately evident that the peaks are well separated, implying an energy gap. The disorder scattering is considerably less than with the ND model [Fig. 1(a)]. In particular, the main peak is sharper in both the Γ_1 and Γ_{15} spectra. In Fig. 3 we plot the separation of the Γ_1 and Γ_{15} peaks as a function of Ge concentration (solid line joining filled circles). In general, there is good agreement between our calculated gap and the experimental data.¹¹ The theoretical curve is deeply bowed, but it does not show a discontinuous slope, as in the ND and DR models.

At large Ge concentrations, where our model gives significant concentrations of antisites, we may examine their effect. The dashed curve in Fig. 3 was obtained from clusters that were generated according to our model and then modified by converting antisite occupancy to site occupancy. It is evident that antisites *per se* do not have a significant effect upon the energy gap. In contrast, we found that calculations for the ND model at $x=0.5$ were dependent on the presence or absence of antisites.

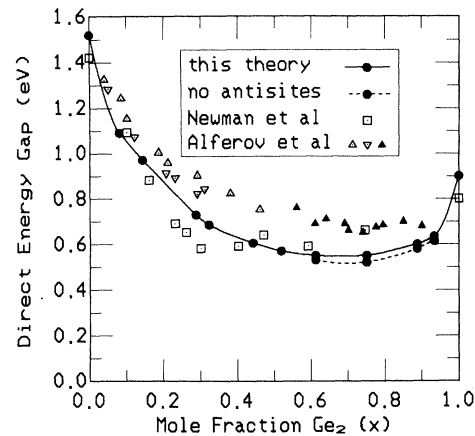


FIG. 3. Calculated and experimental energy gaps for $(\text{GaAs})_{1-x}\text{Ge}_{2x}$. The solid curve corresponds to our model and the dashed curve was obtained after eliminating antisite disorder. The unconnected points are experimental values from Refs. 1 and 4. (See also Ref. 11.)

Thus, conversion of the antisites to sites gave a gap of 0.5 eV instead of the zero value shown in Fig. 1(a). This different behavior arises as follows. At $x=0.5$ the percolation probability for GaAs is approximately 0.8 (for a simply substituted diamond lattice that corresponds to the ND model). This implies that an antisite fraction of up to about 0.1 can arise from random orientation of isolated GaAs clusters. The antisite fraction in the ND model is 0.5 for $x \geq 0.3$ and this implies the presence of a significant concentration of Ga-Ga and As-As NN pairs. In the tight-binding model the isolated As antisite in GaAs has an A_1 level at 0.6 eV above the valence band, which is close to the value 0.52 eV given by Weber *et al.*¹² When the As-As NN pair concentration becomes large, the A_1 levels broaden into a band that overlaps both conduction- and valence-band edges (near $x=0.5$). Ga-Ga NN pairs have less influence on the gap because the Ga antisite does not give a level in the GaAs gap, at least within our model.

We conclude that the direct energy gap of $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ is consistent with a simple statistical model for the crystal lattice in which GaAs occurs randomly as Ga-As NN pairs and in which Ga-Ga and As-As NN pairs are forbidden. While antisite disorder is predicted for Ge-rich alloys, this and the associated change from the zinc-blende to the diamond structure have negligible influence on the magnitude of the direct energy gap.

At present, we cannot exclude the possibility that our model is somewhat oversimple. Because of uncertainties in the tight-binding description, models

with more complicated lattice statistics might be consistent with the observed energy gap. However, application of Occam's razor suggests that such complications, if needed, should only be introduced in response to definitive experimental information about NN environments in the alloy.

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⁵K. E. Newman and J. D. Dow, *Phys. Rev. B* **27**, 7495

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⁶R. Haydock, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1976), Vol. 35, p. 215.

⁷L. C. Davis, *Phys. Rev. B* **28**, 6961 (1983).

⁸K. E. Newman, private communication.

⁹We have examined the effect of using other published parameter sets. [E.g., D. J. Chadi, *Phys. Rev. B* **16**, 790 (1977).] These were discarded because they failed to give reasonable energies for the As antisite in GaAs.

¹⁰H. L. Frisch, J. M. Hammersley, and D. J. A. Welsh, *Phys. Rev.* **126**, 949 (1962).

¹¹Data from Ref. 1 are for layers grown by pyrolysis at 700–750 °C and include those that were attributed to an indirect gap. (We find that the gap remains direct for $x \leq 0.97$.) The data from Ref. 4 appear to be a partial revision of data in Ref. 2, which pertain to layers grown at 450–550 °C by sputtering with simultaneous ion bombardment. The difference between the two sets of data may not be significant because of uncertainties in the extrapolations that were used to derive the gaps.

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