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Two Disordered Phases of the β-Tin Structure in Binary Semiconductors

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The Ising model on a β-tin structure has a phase diagram containing three distinct phases involving order, disorder, and a frustrated ordering. The x-ray crystallographic observation that no ordered β-tin phases exist at room temperature in compound semiconductors may indicate either "paramagnetic" (dynamic) or frustrated (static) disorder. Density functional pseudopotential calculations determine which regimes real materials fall into and predict that in materials such as GaSb, there may be two temperature-driven transitions between β-tin structures: from ordered, to frustrated order, to disordered.

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The high pressure crystal structures of most III-V binary compounds can generally be understood by ordering of anions and cations on underlying lattices based on the high pressure phases of silicon and distortions therefrom [1,2]. For any covalent structure containing only even membered rings of bonds, such as diamond, lonsdaleite, simple cubic (SC), and body-centered cubic or BC8, a unique ordering which maximizes the number of unlike nearest neighbors can be made. In the above cases these structures are zinc blende, wurtzite, rocksalt, CsCl, and SC16, respectively, all of which are observed in binary compounds [1,2].

For structures containing odd membered rings, formation of binary equivalents is more difficult. Some pairs of dissimilar neighbors are inevitable, and it is rare that there is a unique way to minimize their number. This leads to a frustration and the absence of binary equivalents of the β-tin [3], simple hexagonal [4], or SC16 [5] structures among fully ionic materials.

In the high pressure phases of the III-V compounds covalent bonding is still the dominant mechanism for cohesion, and many structures based on the β-tin or simple hexagonal lattice are observed. One would expect that the ionic contribution to the bonding would lead to the stabilization of some ordered structures, and indeed three structures based on different orderings of simple hexagonal (each of which maximizes the number of unlike nearest neighbors) have been reported. For β tin, however, although the underlying covalent structure is observed in a number of materials, *no binary ordered phase has been observed* [3].

In this paper we investigate further the nature of ordering on the β-tin lattice using a next-nearest neighbor antiferromagnetic Ising model, the Hamiltonian for which is

$$H = \sum_{l} \sum_{i=1}^{8} \left[\sum_{j=1}^{4} J\sigma_{i,l}\sigma_j + \sum_{k=1}^{2} K\sigma_{i,l}\sigma_k \right].$$

Here i runs over the basis of an eight-atom unit cell of lattice sites, l denotes the cell (see Fig. 1), $\sigma_{i,l} = \pm 1$ denotes one or other species, and the sums run over its four nearest neighbors j and the two next neighbors k as determined from the β-tin lattice. J and K are coupling constants which for the present systems will generally be positive (i.e., the system favors unlike neighbors).

The case of binary ordering arguably provides a better realization of an Ising system than do systems of magnetic spins, since the system has exactly two states and there is no ambiguity in defining a unique crystallographic direction.

The simulation proceeds by exchanging pairs of σ_i according to a Metropolis algorithm under the stoichiometric constraint of conservation of species.

$$\sum_{i,l} \sigma_{i,l} = 0 .$$

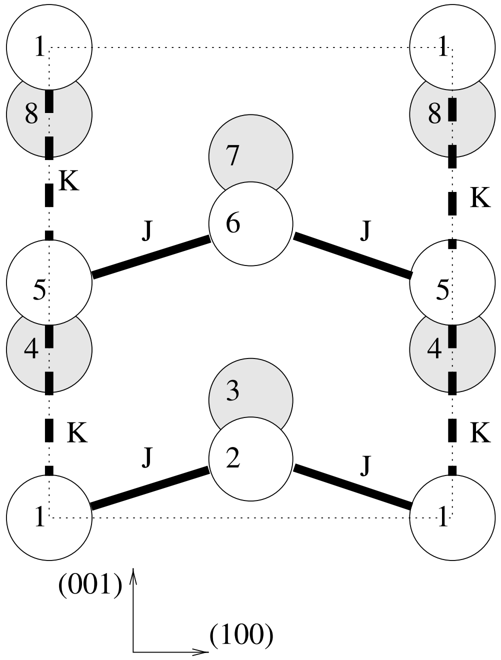

FIG. 1. Diagram of an eight-atom cell of β tin. The (010) direction perpendicular to the paper is identical to the (100). The shaded atoms lie half a unit cell below the face, while the white atoms lie on the cell face. The solid lines connect nearest-neighbor atoms and correspond to bonds with energy J, while the dashed lines correspond to second neighbor bonds with energy K.

In the limit $K = 0$ this model system reduces to fourfold coordination: the nearest neighbor antiferromagnetic Ising model on the diamond lattice, the ground state of which is the zinc blende structure. However, for nonzero K there are five membered rings of connected neighbors, which have been shown to give exotic phase behavior in other lattices [6–8]. In the limit where $K/J = 0.5$ there are multiple equivalent minima which introduce frustration into the system.

The specific heat capacity is monitored (from the time fluctuations in the energy) to determine when a phase transition occurs. The specific heat is defined by

$$C^2 = (\langle H^2\rangle - \langle H\rangle^2)/T^2.$$

Peaks in the specific heat, indicating the presence of phase boundaries, were located in two ways, first moving vertically in $K/J - T$ space by selecting a value for K, and steadily increasing the temperature in steps of $0.02/k_B$. Alternately, moving horizontally in $K/J - T$ space the temperature was held constant, and the coupling parameter K was varied in steps of 0.02. In all cases the coupling parameter J was held fixed at $J = 1$: this effectively sets the temperature scale as discussed below. The calculations were carried out on a $10 \times 10 \times 14$ lattice (5600 sites) using 10^9 swaps between each incremental change of temperature or K/J.

In each case, a distinctive peak in the specific heat capacity was observed at each phase boundary. Moreover, all runs at temperatures above 1.1 had two peaks, indicating that they passed through two phase boundaries (see Fig. 2). The positions of the phase lines are shown in Fig. 3: note that peaks in the heat capacity are not conclusive evidence of a "true" phase transition in the strictest sense.

The experimental signature of ordering in β tin in powder x-ray crystallography experiments is the presence of (110) and (310) difference peaks [3]. Defining the position in fractional coordinates of site i to be r_i, the equivalent order parameter in our simulations is

$$O = \sum \sigma_i \exp[-i\mathbf{r}_i \cdot (110)],$$

which takes the value ± 1 for the zinc blende ordered phase. In practice O is nonzero only in the ordered phase in the bottom left of Fig. 3. Hence either of the other two phases is consistent with the experimental situation where no difference peaks are observed.

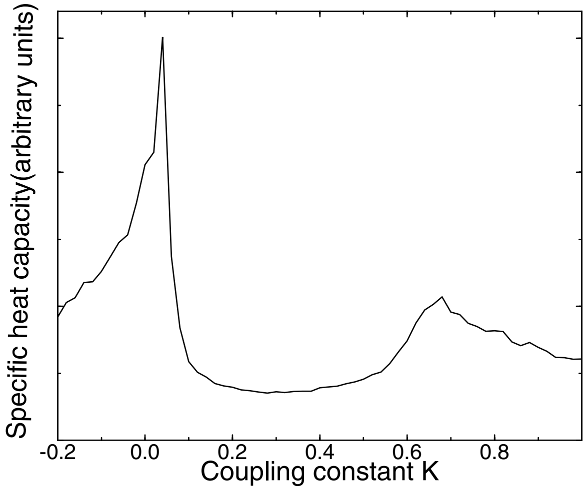

FIG. 2. Typical graph of specific heat capacities (SHC) as a function of coupling parameter K at $T = 1.3$. The peaks in the SHC are taken to indicate the phase transition.

Only one phase has a nonzero ordering parameter corresponding to the absent diffraction peak: this is labeled as the "ordered" phase. The other two are identified as "frustrated" (low temperature) and "disordered" (high temperature) phases: the latter corresponds to a paramagnetic phase and the former to frustrated ordering. In the context of III-V semiconductors the high temperature phase corresponds to a conventional disordered alloy, while the low temperature disordered structure is a more complex state arising from frustrated ordering and the presence of multiple energy minima.

The negative slope of the graph between ordered and frustrated phases arises because of the higher entropy of the latter. This in turn arises because there are many degenerate minima corresponding to the frustrated phase. However, in our finite Monte Carlo simulation we may not be able to sample all of these (indeed at $T = 0$ we sample only one). This leads to large hysteresis and our inability to determine the phase line below about $T = 0.4$, although the Clausius-Clapyron relation suggests it must still have negative slope. The line we actually calculate

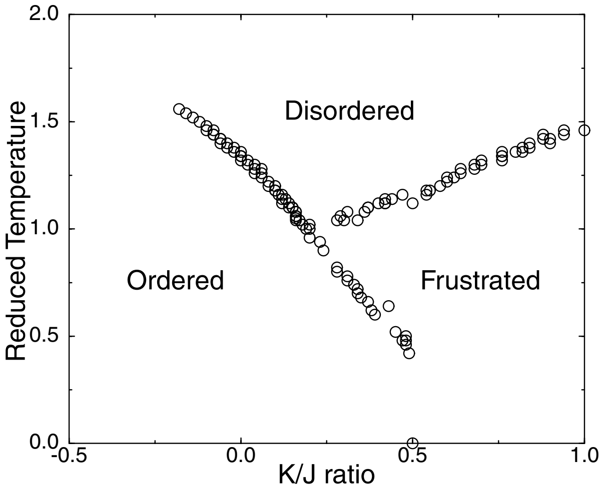

FIG. 3. Phase boundaries for second neighbor stoichiometric Ising model on a β-tin lattice. Boundaries are determined by peaks in the specific heat capacity during runs of gradually increased temperature at constant second neighbor coupling K, and runs of gradually increased K at constant temperature. The circle symbols are approximately equal in size to the resolution of the calculations. J is held constant at $J = 1$ throughout—mapping of reduced temperature to real temperature is discussed in the text.

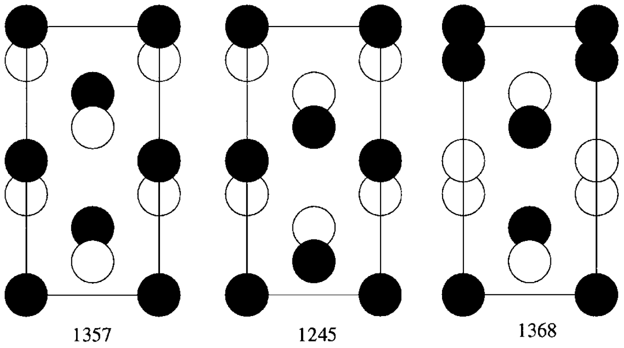

FIG. 4. Schematic drawing showing the three different orderings on the β-tin lattice used in density functional theory calculations for determining the relative energies of nearest and next-nearest neighbor bonds.

tends to $K/J = 0.5$ at the point where measurement becomes impossible. Presuming a vertical phase line from there to $T = 0$ suggests that below this temperature our Monte Carlo procedure samples only one of the frustrated minima, and hence the measured entropy difference becomes zero [9].

The model calculations produce a generic phase diagram (Fig. 3) as a function of temperature and K/J. Different compounds can be mapped onto different K/J values, and application of pressure to a particular compound also has the effect of shifting K/J.

In order to map this generic phase diagram onto real materials, we have carried out *ab initio* ultrasoft [10] pseudopotential calculations using Perdew-Wang exchange correlation [11] on three different decorations of the β-tin lattice [12] at ambient pressure as shown in Fig. 4. In each case the calculation uses an eight-atom cell with a Brillouin zone sampling on a $7 \times 7 \times 9$ k-point mesh, otherwise following the methods described in detail by [4]. The decorations have, respectively,

$$H_{1357} = E_0 - 32J + 16K,$$

$$H_{1256} = E_0 - 16K,$$

$$H_{1368} = E_0 - 16J - 16K,$$

where E_0 represents all terms in the total energy which are the same for each decoration. The supercells used are shown in Fig. 4 where the numbers represent the relative height of the cations in units of $\frac{1}{8}$ of the cell, e.g., 1357 represents the zinc blende ordering.

In all cases we have allowed the ionic positions and unit cell parameters to relax, breaking strict tetrahedral symmetry in cases where than structure is mechanically unstable—thus our calculation encompasses ordered/disordered *Imma* phases [1] as well as true β-tin ones. This method enables us to incorporate short range, but not long range atomic relaxations into the Monte Carlo.

The interpretation of K and J in these cases is rather subtle: They are not the strength of the bond; rather they represent the *difference* in strength between an unlike-neighbor bond and a like-neighbor bond. In almost all cases, they are positive indicating a preference for unlike first and second neighbors. Only in InSb are like-species second neighbors preferred.

Using these calculations and the expressions for H_{1357} etc. given above, we find values for J and K for various III-V semiconductors as given in Table I. We see that in each case the zinc blende style ordering is preferred, and hence all these materials (except AlAs) have $K/J < 0.5$. This suggests that all the materials should exhibit the ordered β-tin phase at sufficiently low temperatures, and several should exhibit both the high temperature entropic disorder and the low temperature frustrated ordering type, passing through two temperature-induced phase transitions.

The mapping of the Ising temperature onto real systems is also not straightforward. The reduced temperature in Fig. 3 is scaled by the value of J; hence the actual transition temperature for a real material (within this model) is given by $T_{\text{trans}} = JT/k_B$, so, for example, GaSb, with $K/J = 0.31$ and $J = 0.0036$ eV, has a transition from ordered to frustrated at reduced temperatures of $T \approx 1.5$ and from frustrated to disordered at $T \approx 2.2$; these temperatures translate to 62 and 92 K, indicating that under ambient conditions β-tin structure GaSb would be disordered but may undergo two phase transitions on cooling.

To investigate whether pressure has any bearing on K/J we examined energetics of GaSb, a material close to the

TABLE I. Calculated cohesive energies, in eV per eight-atom cell, relative to the isolated atoms, for the three decorations of the β-tin structure for various III-V compounds. Also given are the deduced values of J and K.

	H_{1256} (eV)	H_{1368} (eV)	H_{1357} (eV)	J (eV)	K (eV)
AlAs	−32.705	−34.260	−34.235	9.716×10^{-2}	4.936×10^{-2}
AlSb	−29.781	−30.822	−30.944	6.506×10^{-2}	2.873×10^{-2}
GaP	−31.744	−32.631	−32.732	5.542×10^{-2}	2.456×10^{-2}
GaAs	−29.847	−30.385	−30.510	3.362×10^{-2}	1.291×10^{-2}
GaSb	−27.433	−27.972	−28.174	3.365×10^{-2}	1.052×10^{-2}
InP	−28.739	−30.270	−30.423	9.567×10^{-2}	4.306×10^{-2}
InAs	−27.900	−28.077	−28.808	1.106×10^{-2}	-1.731×10^{-2}
InSb	−26.567	−26.863	−27.046	1.855×10^{-2}	0.355×10^{-2}

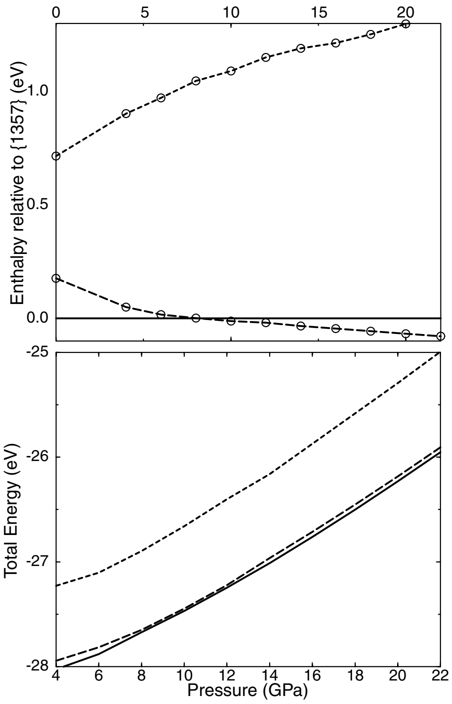

FIG. 5. Lower: variation of energy with pressure of three decorations of the β-tin lattice for GaSb. Dotted line is H_{1256}, dashed line is H_{1368}, and solid line is H_{1357}. Upper: Variation of enthalpy with pressure of three decorations of the eight-atom β-tin lattice for GaSb relative to H_{1357}. Dotted line is H_{1256}, dashed line is H_{1368}, and solid line is H_{1357} (zero). The line crossing suggests a 0 K transition from H_{1357} to H_{1368} ($K/J = 0.5$) at about 8 GPa.

frustrated phase boundary and one in which a disordered β-tin phase has been observed experimentally. We find that the difference between the orderings (and hence K/J) is sensitive to increasing pressure (Fig. 5), with H_{1368} becoming more favorable, possibly because its more complex structure allows changes in internal parameters and compression by buckling [2].

The possibility of a structural transition to a topologically distinct phase, as opposed to a small distortion from β tin, is ignored. However, the existence of β-tin and *Imma* phases both stably and metastably in a range of III-V compound make it plausible that both the spin-glass and disordered structures could be observed.

In summary, we have shown that within the connectivity of the β-tin structure, three possible phases exist, depending on temperature and the relative strength of the first and second neighbor interactions. Pseudopotential calculations suggest that some of the III-V semiconductors, which are known to exhibit the β-tin and related structures, fall into the region where they are able to sample all three ordering regimes as a function of temperature.

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[12] The decorations mean that the various structures have different symmetry and are therefore only "β tin" in a topological sense of having four near neighbors and two second neighbors. Relaxation of the ions and lattice parameters is allowed, to describe the local relaxation, and the total energy (not the enthalpy) is used for H.