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Studies of Ordering in Semiconducting and Other Alloys

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UNDER THE DIRECTION OF

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Studies of Ordering in Semiconducting and Other Alloys

We summarize first in Sec. I our goals, then in Sec. II. our accomplishments, and describe in Sec. III the work in progress at the end of the contracted period which is carried on under ONR Contract No. N00014-91-J-1062. The papers referred to in the text can be found in Sec. IV; this section summarizes material submitted in the annual Publications/Patents/Honors Reports.

I. GOALS OF STUDY

New ordered compounds derived from semiconductor and metallic alloys for special values of the composition x were studied. The types of ordered compounds were cataloged. A goal was to determine the stability of the new ordered states for both low and high temperatures. The properties of both the new stable and metastable compounds, e.g., band gaps were determined. Finally, the validity of a micro-structure model of metastable alloys was tested.

II. ACCOMPLISHMENTS OF STUDY

Properties of New Ordered Compound: Structural Properties

We have determined the structural properties of a number of new ordered compounds using a valence-force-field (VFF) model of strain [P3]. Specifically, we have determined such quantities as strain energies, bond lengths, and dimensions of unit cells. The theoretical framework is particularly of use when combined with further studies, see below.

Properties of New Ordered Compound: Electronic Properties

Note, the work described here was the bulk of the Ph.D. dissertation of Dr. Dan Teng, who is now a post-doctoral research associate at Cornell University.

We have completed the development of an empirical tight-binding (TB) method for the calculation of the electronic structures of the five types of ternary compounds: (0,0,1) and (1,1,1) superlattices, chalcopyrite, famatinite, and luzonite [P1, P2, P5]. Our calculations employ a simple empirical tight-binding Hamiltonian based on an extension of the empirical tight-binding model of Vogl et al. to include two next-nearest-neighbor and two spin-orbit

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interactions. We also incorporated our VFF work to account for the effects of strain distortions [P3].

One of the more interesting results from these calculations was the effect of the crystal field due to strain on the splitting of the top of the valence-band edge. From our VFF model of strain [P3], we know that there are both external (tetragonal and other) and internal distortions within the crystal structure of an ordered semiconductor compound. The three discrete levels E_0 , E_1 , and E_2 at the top of valence bands calculated from our TB model can be decomposed into terms originating from spin-orbit interaction, Δ_{so} , and from the crystal field, Δ_{cf} . As was done for chalcopyrite compounds in the quasicubic-crystal-field model, the crystal-field splitting is expressed in terms of a deformation potential associated with the p orbitals, b_p . We then find the interesting result that the crystal-field splitting Δ_{cf} scales nearly linearly with the tetragonal distortion c/a for common-anion compounds but scales instead *nonlinearly* with the *internal* distortion parameter c_2/c_1 for *common-cation compounds* [P5]. We believe that this result will stimulate experimental studies of deformation parameters for the ordered III-V ternary families.

Micro-Structure Model of Alloys

Strain models derived from ordered materials are found to describe quite well the bond lengths of *alloys*. Comparison is made with experimental results from the EXAFS technique. Excellent results are found for the $Ga_{1-x}In_xAs$ [P3] and for $Hg_{1-x}Cd_xTe$ [P4]. In the latter work, bond lengths were also calculated in collaboration with the Dow group using first-principles techniques; more accurate results were found from our valence-force-field calculations.

Alloy bowing of the band gap

Also studied as part of the Ph.D. dissertation work of Dr. Dan Teng was the extent to which the band gaps of alloys compared with those for ordered compounds [P1, P2, P5]. In this work, comparison was made to results from the virtual-crystal approximation (VCA), from experiment for the alloy, and from experiment (when known) for the ordered compound.

We find that the bowing of the alloy band structure is very slight for an alloy family that shares a common anion and also that the band gaps of the related ordered compounds are generally almost the same as those found for the alloy. In opposition to the common-anion compounds, the offset correction for common-cation compounds causes a significant change in the calculated value of the band gap. Strain effects [P3] are large in this family of compounds.

Large differences between results for band gaps from VCA theory and ordered compounds are typically found. Interestingly, the experimental alloy bowing of the direct gap for metastable alloys such as $\text{GaAs}_{1-x}\text{Sb}_x$ almost passes through these points found for certain ordered structures. There exists a possibility, unconfirmed as yet, that the bowing of the band gap some metastable alloys is due to the incipient existence of alloy ordering.

III. WORK IN PROGRESS AT END OF PERIOD

Exotic Ordered States of Cubic and Hexagonal Symmetry:

The familiar semiconductors studied today have either diamond, zinc-blende, or wurtzite crystal structures, e.g., Si, GaAs, and CdS. Binary, ternary, and quaternary alloys combine two or more of these materials, e.g., conventional alloys such as $\text{Si}_x\text{Ge}_{1-x}$ and $\text{GaAs}_x\text{P}_{1-x}$ and unconventional alloys such as $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ and $\text{CdTe}_{1-x}\text{S}_x$. These alloys should be thought of as potential parents to new ordered structures. A catalog of ordered structures derived from zinc-blende or wurtzite parents can be assembled from the known ground states of face-centered cubic (fcc) or hexagonal-close packed (hcp) materials. Possible ordered states of a ternary "disordered-cation" alloy $\text{A}_{1-x}\text{B}_x\text{C}$ having zinc-blende structure include those in which the cations order on their fcc sublattice.

By modeling the chemical energy of a semiconductor in terms of an Ising model

$$E = - \sum_k \sum_{\langle ij \rangle_k} J_k S_i S_j - H \sum_i S_i$$

the ground-state structures of a fcc material can be determined, as a function of the k-th neighbor interaction energies J_k . (In this equation, S_i is the spin of a lattice point i , H an external magnetic field, and the sum over $\langle ij \rangle_k$ is over the k-th neighbor pairs of spins.) The ordered ground-state structures are found to assemble into families which are sorted by common type of ordering wave vector k [M1]. Strain energies for these ordered compounds are also found to sort into families characterized by a common ordering wave vector k [M1].

We believe that the grouping of ordered semiconductors into families by wave vector k is a concept that should be useful beyond simple studies of strain. Trends should follow general symmetries and not from details of the calculations; e.g., the sets of possible ordered "daughter/son" compounds of either zinc-blende or wurtzite parents follow generally from group theory.

Studies of Exotic Alloys:

Given the basic question of whether the new ordered ternary III-V compounds are equilibrium or metastable phases of the alloy, it is important to understand first semiconductor phase transitions that occur clearly at equilibrium. The (chalcopyrite)-(zinc-blende) system is natural to study for two reasons. First, many natural chalcopyrite compounds exist in nature, with many of them undergoing an equilibrium order-disorder transition as a function of temperature between the chalcopyrite to zinc-blende crystal types. Second, the anion sublattices of the chalcopyrites are "unmixed" and monoatomic; the anion is from the same column of the Periodic Table as the anion in the related "parent" zinc-blende compound. Thus "mixed" (chalcopyrite)-(zinc-blende) alloys are easily grown.

We have found recently that the ordered phases of these alloys are well described by a generalized anti-ferromagnetic Blume-Emery-Griffiths model [M3]. Equilibrium phase diagrams of this model are calculated in the tetrahedron approximation of the cluster variational method. Our calculated phase diagrams compare quite favorably with ones from experiment for the two DMS systems $(\text{CuIn})_{1-x}\text{Mn}_{2x}\text{Te}_2$ and $(\text{AgIn})_{1-x}\text{Mn}_{2x}\text{Te}_2$.

Further Strain Studies: $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$

We are continuing our study of the strain properties of other semiconductor systems by studying the diluted magnetic semiconductor (DMS) $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$. These alloys are grown at Notre Dame in both bulk and epitaxial form by Furdyna's group. Particularly interesting is the question of spontaneous versus artificial order. A technique is being developed, the Random Cluster Iteration Method [M2], to study the effect of randomness on strain. At present time, it appears that $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ is more random than ordered.

Calculations of optical spectra for GaInP_2

In progress at the time of completion of the contract was the development of a new computer code which used our band-structure technique [P1, P2, P5] to calculate the optical spectra of the new ordered compounds. In particular, we have calculated the imaginary part of the dielectric constant ϵ_2 by convolving the integral for the joint density of states with an expression from Harrison for the oscillator strength. An initial comparison of our calculations to the photoluminescence data of the (1,1,1) superlattice of GaInP_2 , has yielded good qualitative agreement with experiment [M4]. We expect that calculations such as these will be of considerable use to experimentalists.

IV. ACTIVITY SUMMARY

Papers published in refereed journals

- P1. K. E. Newman, J. Shen, D. Teng, B.-L. Gu, S.-Y. Ren, and J. D. Dow, "Electronic and Structural Properties of Ordered III-V Alloys," refereed, Alloy Phase Stability, Eds. G. M. Stocks and A. Gonis, p. 621-625 (Kluwer, Dordrecht, 1989). (Other support, for Dow, N00014-84-K-0352 and AROSR-85-0331).
- P2. K. E. Newman, D. Teng, J. Shen, and B.-L. Gu, "Electronic and Structural Properties of Ordered III-V Alloys," refereed, Band Structure Engineering in Semiconductors, Ed. R. A. Abram and M. Jaros, p. 119-127 (Plenum, NY, 1989). (Other support, for Shen, N00014-84-K-0352 and AROSR-85-0331.)
- P3. K. E. Newman, J. Shen, and D. Teng, "Effects of Strain on Structural Properties in Ordered Semiconductors," Superlattices and Microstructures **6**, 245-257 (1989).
- P4. M.-H. Tsai, J. D. Dow, K. E. Newman, and R. V. Kasowski, "Theory of Bond-Length Relaxation in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ Alloys," Phys. Rev. B **41**, 7744 (1990).
- P5. D. Teng, J. Shen, K. E. Newman, and B.-L. Gu, "Effects of Ordering on the Band Structure of III-V Semiconductors" (submitted and since published in J. Phys. Chem. Solids **52**, 1109-1128 (1991). (Other support, for Newman, DARPA N0530-0716-05, and, for Shen, N00014-84-K-0352 and AROSR-85-0331.)

Manuscripts in preparation at time of termination of contract

- M1. J. R. Gregg and K. E. Newman, "Effects of Symmetry on the Strain Energy of Ordered Semiconductors."
- M2. M. R. Weidmann, J. R. Gregg, and K. E. Newman, "Calculations of Local Structural Properties of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ Alloys: The Random Iterative Cluster Model."
- M3. K. E. Newman and X. Xiang, "Calculations of Phase Diagrams for Semiconducting (Chalcopyrite) $_{1-x}$ (Zinc-Blende) $_{2x}$ Alloys."
- M4. D. Teng and K. E. Newman, "Calculations of the Optical Spectra of (1,1,1)-Ordered GaInP_2 ."
- M5. J. Ni, B.-L. Gu, K. E. Newman, "The Structure of the Alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ and its Electronic Properties."

Invited presentations at topical or scientific/technical society conferences

- I1. K. E. Newman, "Structural and Electronic Properties of Ordered Semiconductors," 1989 Electronic Materials Conference, M.I.T., Cambridge, June 22, 1989.
- I2. "The Effects of Ordering in Semiconductor Alloys," seminar at Purdue University, September 29, 1989.

Contributed presentations at topical or scientific/technical society conferences

- C1. J. R. Gregg and K. E. Newman, "Strain Energy and Bond-Length Calculations in DMS Alloys," March 1989 APS meeting, St. Louis, March 21, 1989 (Other support, DARPA under N0530-0716-05).
- C2. D. Teng and K. E. Newman, "Electronic Structure of Ordered Ternary III-V Alloys," March 1989 APS meeting, St. Louis, March 23, 1989.
- C3. X. Xiang and K. E. Newman, "Equivalence of the Two Formulations of the Cluster Variational Method," March 1989 APS meeting, St. Louis, March 21, 1989.
- C4. M. R. Weidmann, K. E. Newman, and J. R. Gregg, "Strain Energy and Bond-Length Calculations in $Zn_{1-x}Mn_xSe$ Alloys," March 1990 APS meeting, Anaheim, CA, March 15, 1990 (Other support, DARPA under N0530-0716-05).
- C5. D. Teng and K. E. Newman, "Calculation of the Electroreflectance Spectrum of the $(GaP)_1/(InP)_1$ (111) Strained-Layer Superlattice," March 1990 APS meeting, Anaheim, March 14, 1990.
- C6. K. E. Newman, M. R. Weidmann, and J. R. Gregg, "Structural Properties of $Zn_{1-x}Mn_xSe$ Alloys," Sixth International Conference on X-Ray Absorption Fine Structure, York, England, August 8, 1990.

Graduate Students and Postdoctorals Supported

- G1. Dr. Jeffrey R. Gregg
- G2. Mr. Dan Teng (Ph.D., September 1990)
- G3. Mr. Xiaou Xiang (Masters, June 1990)
- G4. Mr. Matthew Weidmann