Ab Initio Determination of a Structural Phase Transition Temperature

K. M. Rabe and J. D. Joannopoulos
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 7 October 1986)

The temperature of the structural phase transition in GeTe is calculated completely *ab initio* from a model lattice-dynamical Hamiltonian that is constructed from microscopic quantum-mechanical total-energy calculations. The phase transition in the model system is studied through a renormalization-group–theory approach, leading to the prediction of a fluctuation-driven first-order transition at 657 ± 100 K.

PACS numbers: 64.70.Kb, 63.75.+z, 71.45.Nt

In the application of modern concepts of critical phenomena to the study of finite-temperature phase transitions in real materials, the calculation of the transition temperature and other nonuniversal critical properties is essential. This requires the combination of detailed microscopic quantitative knowledge of the properties of the material under consideration with an appropriate statistical-mechanical treatment.

One way to obtain these properties is through first-principles total-energy calculations. Previous attempts to calculate transition temperatures[1,2] have used total-energy methods which rely on approximations limiting their accuracy and range of applicability. In contrast, the *ab initio* pseudopotential method has been seen to be highly accurate in describing the zero-temperature structural properties of a wide variety of systems,[3] including group-IV tellurides.[4] In the present study of the structural phase transition of bulk GeTe, we combine this self-consistent method with a renormalization-group–theory approach to calculate T_c and predict other critical phenomena associated with the transition, in excellent agreement with available experimental data.

At high temperatures, the IV-VI narrow-gap semiconductor GeTe has the rock-salt structure. At low temperatures, the system exists in a rhombohedral structure. This structure, shown in Fig. 1, can be described as a rock-salt structure slightly distorted by the freezing in of a $\mathbf{k}=\mathbf{0}$ optic phonon along the [111] direction, corresponding to the order parameter of the transition, with a subsequent shear relaxation along [111]. For various reasons, experimental studies of the transition and their interpretation are somewhat difficult. Observed transition temperatures range from 625 to 700 K.[5-7] In some measurements,[7] small discontinuities in volume and α have been detected at the transition, suggesting that it may be weakly first order.

Our theoretical investigation of this transition proceeds in three steps: (1) manipulation of the full anharmonic lattice Hamiltonian into a form with a tractable number of coupling constants (fifteen) to be determined by (2) pseudopotential total-energy calculations for various structural configurations, and finally (3) a renormalization-group calculation implemented in momentum space to obtain T_c and the critical properties associated with the transition.

For the description of a displacive transition[8] such as that in GeTe, an anharmonic lattice Hamiltonian is appropriate.[9,10] The local-mode approximation[11] provides an intuitively appealing way of obtaining an equivalent model Hamiltonian with a greatly reduced number of parameters. For each unit cell, the local-mode variable is defined as the projection of the ionic displacements onto the polarization vectors of the $\mathbf{k}=\mathbf{0}$ optic modes, referred to the mean positions in the high-temperature structure. The Hamiltonian is expanded in symmetry-allowed powers of the local-mode variables, with on-site terms kept up to some arbitrary order and intersite interactions to quadratic order only.

The approximation of purely local anharmonicity, essential for the obtainment of a Hamiltonian with a small number of parameters, necessitates that the precise choice of local mode incorporate a physical understanding of the lattice instability. The charge flow and energy gain that result from the symmetry breaking by the distortion of the six equivalent nearest-neighbor bonds of the rock-salt structure involves primarily Te p-like states,[4,12] while the main anharmonic contribution to the energy originates in the nonlinear Te polarizability.[13] Thus for GeTe the best choice of local mode emphasizes the distortion of the Te-ion environment:

$$\xi_i = a_0^{-1}\left(\Delta \mathbf{r}^i_{\mathrm{Te}} - \sum_{\mathrm{nn}j} \Delta \mathbf{r}^j_{\mathrm{Ge}}/6\right),$$

where a_0 is the length of the side of the fcc conventional

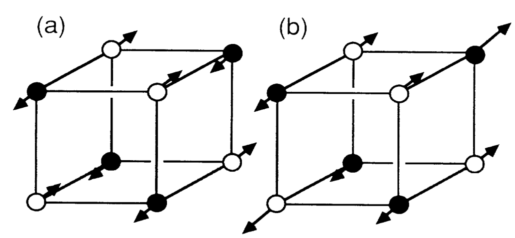

FIG. 1. The low-temperature rhombohedral structure of GeTe as a two-step distortion of the rock-salt structure.

unit cell and the displacements $\Delta\mathbf{r}$ are measured relative to the rock-salt structure.

The local-mode variables sit on the sites of an fcc lattice and only cubic-symmetry invariants appear in the expansion of the Hamiltonian. We truncate the on-site potential at fourth order but keep isotropic terms to eighth order. Intersite interactions up to second order are included since the constraints imposed by the sharing of Ge atoms by first- and second-neighbor local-mode octahedra suggest that the coupling is important.

The general expression for the on-site potential is

$$\sum_i \{A\,|\boldsymbol{\xi}(\mathbf{R}_i)|^2+u_0|\boldsymbol{\xi}(\mathbf{R}_i)|^4+v_0\sum_\alpha \xi_\alpha(\mathbf{R}_i)^4+D\,|\boldsymbol{\xi}(\mathbf{R}_i)|^6+E\,|\boldsymbol{\xi}(\mathbf{R}_i)|^8\},$$

with the intersite interactions

$$-\tfrac{1}{2}\sum_i\Bigg[\xi_x(R_i)\Bigg(a_1\sum_{\mathbf{d}\in\{(\pm\hat{\mathbf{x}}\pm\hat{\mathbf{y}}),(\pm\hat{\mathbf{x}}\pm\hat{\mathbf{z}})\}}\xi_x(\mathbf{R}_i+a_0\mathbf{d}/2)+a_2\sum_{\mathbf{d}\in\{(\pm\hat{\mathbf{y}}\pm\hat{\mathbf{z}})\}}\xi_x(\mathbf{R}_i+a_0\mathbf{d}/2)$$
$$+a_3\sum_{\mathbf{d}\in\{(\pm\hat{\mathbf{x}}\pm\hat{\mathbf{y}})\}}(\mathbf{d}\cdot\hat{\mathbf{x}})(\mathbf{d}\cdot\hat{\mathbf{y}})\xi_y(\mathbf{R}_i+a_0\mathbf{d}/2)+a_3\sum_{\mathbf{d}\in\{(\pm\hat{\mathbf{x}}\pm\hat{\mathbf{z}})\}}(\mathbf{d}\cdot\hat{\mathbf{x}})(\mathbf{d}\cdot\hat{\mathbf{z}})\xi_z(\mathbf{R}_i+a_0\mathbf{d}/2)$$
$$+b_1\sum_{\mathbf{d}\in\{\pm\hat{\mathbf{x}}\}}\xi_x(\mathbf{R}_i+a_0\mathbf{d})+b_2\sum_{\mathbf{d}\in\{\pm\hat{\mathbf{y}},\pm\hat{\mathbf{z}}\}}\xi_x(\mathbf{R}_i+a_0\mathbf{d})\Bigg)+\text{cyclic perm.}\Bigg],$$

where $\boldsymbol{\xi}(\mathbf{R}_i)$ is the local-mode variable at the fcc lattice site $\mathbf{R}_i$.

We also include in the Hamiltonian the lowest-order terms which describe strain deformations and their coupling to the order parameter. With the strain tensor $e_{\alpha\beta}=\frac{1}{2}(\delta u_\beta/\delta x_\alpha+\delta u_\alpha/\delta x_\beta)$, the expression valid for long-wavelength strain fields is

$$(\Omega_0)^{-1}\int d\mathbf{r}\cdot\Bigg(C_{11}\sum_\alpha e_{\alpha\alpha}^2(\mathbf{r})/2+C_{12}\sum_{\alpha\neq\beta}e_{\alpha\alpha}(\mathbf{r})e_{\beta\beta}(\mathbf{r})/2+C_{44}\sum_{\alpha\neq\beta}e_{\alpha\beta}^2(\mathbf{r})$$
$$-g_0\sum_\alpha e_{\alpha\alpha}(\mathbf{r})\xi^2/3-g_1\sum_{\alpha<\beta}e_{\alpha\beta}(\mathbf{r})\xi_\alpha\xi_\beta-g_2\sum_\alpha e_{\alpha\alpha}(\mathbf{r})(\xi_\alpha^2-\xi^2/3)\Bigg).$$

The values of the coefficients for GeTe are obtained by the fit of the model Hamiltonian to the energies of a variety of local-mode configurations. For the zero-strain coefficients A, u_0, v_0, D, E, a_1, a_2, a_3, and b_1+2b_2, we must consider configurations with the full fcc translational symmetry as well as configurations with two translationally inequivalent types of local-mode variables on fcc lattice sites. In each type of unit cell, we study two families of local-mode configurations, specified by a fixed polarization vector at each inequivalent site and a varying amplitude τ. For each family, the energy as a function of τ determines one combination of coefficients at each order.

To obtain the strain coefficients C_{11}, C_{12}, C_{44}, g_0, g_1, and g_2, it is sufficient to consider configurations in which the local mode is uniform and only the lattice changes. We study three types of variations corresponding to pure volume change, pure rhombohedral-angle change at fixed volume, and uniaxial strain e_{zz}.

The calculations of the energies of local-mode configurations are performed[14] with use of scalar relativistic pseudopotentials, a plane-wave basis with cutoff $E_1=10.5$ Ry and Löwdin perturbation up to $E_2=16.5$ Ry, and special $\mathbf{k}$-point sets with up to 343 points in the full Brillouin zone for fcc, 100 for tetragonal, and 125 for rhombohedral. Convergence tests show that with these cutoffs, energy curvatures are determined to about 10% accuracy.

In principle, the local-mode configuration energy is obtained from an integral over the corresponding space of ionic configurations. To a good approximation,[14] it can be taken as the minimum over the corresponding ionic configurations with the same translational and point symmetries as the local-mode configuration. The performance of this procedure for all the local-mode configurations, which in each case involves at most a one-dimensional minimization, results in the energies shown in Fig. 2. The model Hamiltonian parameters obtained from fitting of these energies are given in Table I.

Given this microscopic Hamiltonian, the transition temperature and critical properties follow from the evaluation of the partition function. A systematic approach begins with a Hubbard-Stratonovich transformation on the partition function to introduce a dynamical mean field ϕ_i which couples linearly to the order parameter. The trace over ξ_i is expanded in ϕ_i and e to give a functional of the same form as the original Hamiltonian, where the coefficients are now combinations of single-site traces.

The evaluation of the resulting functional integral within mean-field theory leads to a T_c of 673 K. An estimate of the correction to this value and information about the critical behavior can be obtained through the renormalization group in the ϵ expansion. This type of compressible three-component model with cubic anisotropy has been studied previously.[15] For the present discussion we write the functional in the standard Landau-Ginzburg-Wilson form with $n=3$, $d=3$, and cubic symmetry, including the infinite-range intersite quartic cou-

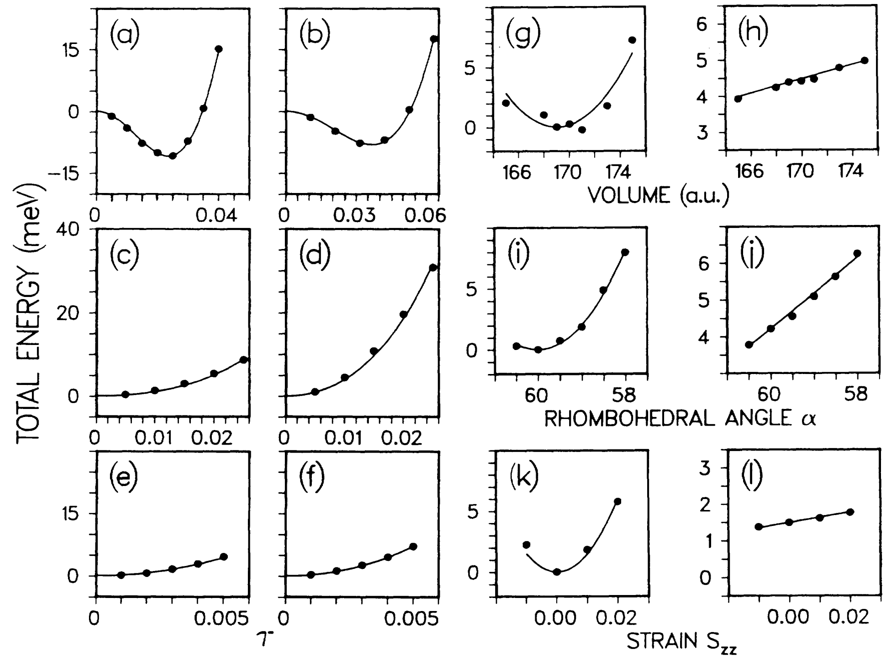

FIG. 2. Calculated local-mode configuration energies, given relative to the rock-salt structure minimum in meV per atom. Solid lines show fit with use of the model Hamiltonian parameters given in Table I. On the left, the energies for six families of local-mode configurations with zero strain are shown—longitudinal and transverse: (a),(b) fcc; (c),(d) tetragonal; (e),(f) rhombohedral. On the right, the energies of configurations which include strain: (g),(i),(k) pure strain distortions, (h),(j),(k) $E(e,\tau=0.01)-E(e,\tau=0.00)$ which determines the order-parameter–strain coupling.

plings generated by integrating out the homogeneous strain. This leads to

$$\beta H_{\mathrm{LGW}}=\int d^3r\Big[[r_0(T-T_{c,\mathrm{mf}})\,|\boldsymbol{\phi}(\mathbf{r})|^2+|\nabla\boldsymbol{\phi}(\mathbf{r})|^2]/2+u\,|\boldsymbol{\phi}(\mathbf{r})|^4+v\sum\phi_\alpha(\mathbf{r})^4$$
$$+O(\phi^6)+\tfrac{1}{2}\Big(f\sum_\alpha(\partial_\alpha\phi_\alpha)^2-h\sum_{\alpha\neq\beta}(\partial_\beta\phi_\alpha)(\partial_\alpha\phi_\beta)\Big)\Big]$$
$$+\int d^3r\int d^3r'\Big\{w_0\sum_\alpha\phi_\alpha(\mathbf{r})^2\phi_\alpha(\mathbf{r}')^2+w_1\sum_{\alpha<\beta}\phi_\alpha(\mathbf{r})^2\phi_\beta(\mathbf{r}')^2+w_2\sum_{\alpha<\beta}\phi_\alpha(\mathbf{r})\phi_\beta(\mathbf{r})\phi_\alpha(\mathbf{r}')\phi_\beta(\mathbf{r}')\Big\}.$$

In analyzing this model, we neglect the higher-order anharmonicities and the anisotropic components of the gradient terms, since these are marginal or irrelevant fields and will modify the flows significantly only in extreme cases. Thus we consider the momentum-space renormalization-group differential recursion relations to first order in $\epsilon=4-d$ in the six-dimensional parameter space $r=r_0(T-T_{c,\mathrm{mf}})$, u, v, w_0, w_1, and w_2. By iterating the recursion relations numerically, we can examine the changes in the flows as the system moves along the line in parameter space according to the physical temperature T, and find a shift in T_c of -16 K, yielding $T_c=657$ K.

TABLE I. Model Hamiltonian parameters for GeTe (electronvolts per local mode).

On site		Intersite		Elastic		Coupling	
A	59.3	a_1	6.08	C_{11}	29.7	g_0	167
u	8.73×10^3	a_2	10.5	C_{12}	0.12	g_1	420
v	4.12×10^3	a_3	4.38	C_{44}	5.75	g_2	134
D	-7.32×10^5	b_1+2b_2	42.0				
E	2.36×10^7						

This renormalization-group analysis can also be used to understand the observed first-order character of the transition. At the fixed points of the pure cubic-anisotropy model ($w_i=0$), the w_i are relevant. There are new fixed points with $w_i^*>0$, but these are not accessible to flows starting in the $w_i<0$ region of parameter space. The resulting runaway behavior of the strain-generated couplings is associated in principle with the occurrence of a first-order transition. To see that this provides a plausible mechanism for the observed character of the transition, consider that within mean-field theory, the effect of the strain coupling is to shift the effective values of (u,v) towards the mean-field phase boundary $u_{\text{eff}}+v_{\text{eff}}/3=0$, from $(u,v)=(0.018,0.013)$ to $(u,v)=(-6.1\times 10^{-4},0.028)$. This substantial shift suggests that though the transition within mean-field theory is still second order, the strain effects could be large enough to produce an observable discontinuity within the renormalization group, and thus the transition is fluctuation-driven first order.

In summary, we have studied the phase transition of GeTe completely *ab initio*, predicting $T_c=657\pm 100$ K. This compares quite favorably with experimental values. In addition, we find that the presence of the order-parameter strain coupling moves the system into the fluctuation-driven first-order region of the phase diagram, consistent with experimental indications of a discontinuous transition. This provides an encouraging prospect for future applications of the pseudopotential total-energy method to the calculation of finite-temperature properties of solids.

We acknowledge valuable discussions with A. N. Berker, A. Aharony, M. Kardar, and D. Blankschtein. One of us (K.R.) thanks AT&T Bell Laboratories for support. This work was supported in part by U.S. Office of Naval Research Contract No. N0014-86-K-0158.

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