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Structural properties of GeTe at $T=0$

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The equilibrium lattice parameters, bulk modulus, shear elastic constant C_{44}, and cohesive energy of GeTe are calculated with use of the *ab initio* scalar relativistic pseudopotential in the local-density approximation. The convergence of the structural properties in basis-set size and Brillouin-zone averaging is discussed. For the rocksalt structure, valence charge densities and the band structure are presented. For the rhombohedral structure, the band structure is presented and the shear deformation potential is calculated. Good agreement of calculated quantities with available experimental results is obtained.

I. INTRODUCTION

The structural properties of the group-IV tellurides GeTe, SnTe, and PbTe are of interest because these compounds have a lattice instability which results in a rocksalt-rhombohedral transition at finite temperature for SnTe and GeTe. Recently we reported the application of the *ab initio* pseudopotential total-energy method to the study of the structural properties of the IV-VI compounds SnTe and PbTe at $T=0$.[1] Here we present the extension of this work to the analogous compound GeTe. In particular, we discuss calculations of the lattice constant, bulk modulus, cohesive energy, total charge density, and band structure for the high-temperature rocksalt form, and then study the distortions corresponding to the observed low-temperature rhombohedral structure and resulting changes in the band structure. This work forms the foundation of an *ab initio* study of the structural transition in GeTe, to be reported elsewhere.[2]

The format of this paper is as follows. In Sec. II we give information about the computation of total energies and band structures. In Secs. III and IV we give the results of calculations in the rocksalt and distorted structures, respectively. Section V contains a discussion of various issues pertaining to the calculations and their interpretation, and concluding remarks.

II. METHOD

As described previously,[1] we obtain quantum-mechanical total energies of various ionic configurations of GeTe using the self-consistent *ab initio* pseudopotential total-energy method with the local-density approximation (LDA) in the momentum-space formalism. For total energies and self-consistent potentials, we use the spin-orbit–averaged pseudopotentials of Bachelet, Hamann, and Schlüter[3] (Fig. 1), while for band structures the spin-orbit splitting is included. We use the Ceperley-Alder-Perdew-Zunger form[4] for the exchange-correlation potential. Brillouin-zone (BZ) averages are performed using the special-**k**-point scheme of Monkhorst and Pack[5] with $7^3=343$ points in the full BZ. Wave functions are expanded in a basis set of plane waves with energy less than $E_1=10.5$ Ry, while the effects of plane waves with energy above E_1 and below $E_2=16.5$ Ry are included using Löwdin perturbation theory.[6] Computations were performed using an IBM 370/4381 with an 8-byte word length.

III. RESULTS: ROCKSALT STRUCTURE

At temperatures above $T_c \sim 670$ K, GeTe is observed to crystallize in the rocksalt structure.[7,8] By calculating $E(V)$ at various atomic volumes V [Fig. 2(a)] and fitting to a polynomial quadratic in V we can extract the lattice constant and bulk modulus of a hypothetical rocksalt form at $T=0$, given in Table I. After making a rough thermal expansion correction of -1.5% to the experimental lattice constant values also given in Table I, corresponding to a linear thermal expansion coefficient of 20×10^{-6} for $T>T_c$ (Ref. 9), we see that the calculated values are $\sim 1\%$ too small. Though there are no measurements of the bulk modulus for GeTe, the calculated value of 0.51 Mbar is, as expected, roughly the same as measurements in SnTe and PbTe, which fall in the range 0.4–0.5 Mbar.[10,11]

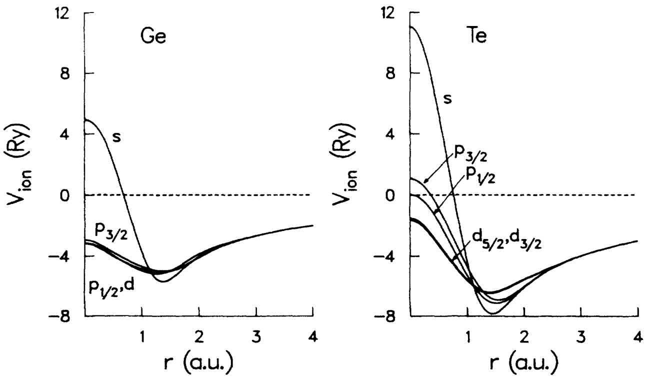

FIG. 1. *Ab initio* nonlocal relativistic atomic pseudopotentials for Ge and Te as calculated by Bachelet, Hamann, and Schluter (Ref. 3).

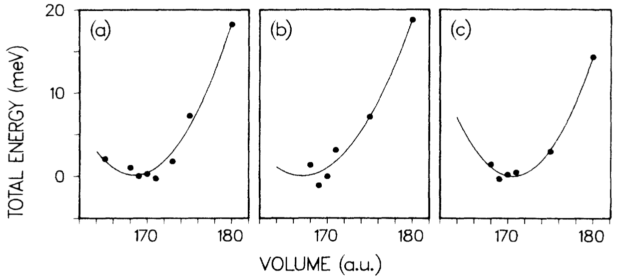

FIG. 2. Total energy of the rocksalt structure, in meV/atom, as a function of varying atomic volume. The points shown are calculated with (a) set-A cutoffs, (b) set-B cutoffs, and (c) set-C cutoffs. For each set, the minimum of the parabolic fit shown as a solid line is selected as the zero of energy.

By calculating the energies of free Ge and Te pseudoatoms, we obtain 6.9 eV/pair for the cohesive energy of GeTe, compared to the experimental value 6.1 eV/pair.[12,13] The overestimate can mostly be attributed to difficulties in calculating the free-atom energy, both from the use of the LDA and from the approximate treatment of the spin-orbit interaction energy, as discussed previously.[1]

In order to study convergence, in addition to calculations with energy cutoffs (10.5,16.5 Ry) and 7^3 **k** points (set A), we include in Fig. 2 and Table I the results of calculations with (10.5,16.5 Ry) and 6^3 **k** points (set B) and (11.5,18.0 Ry) and 6^3 **k** points (set C). The convergence of the lattice constant is excellent. The examination of the convergence of the bulk modulus is complicated by uncertainty in our fitted values, arising from two sources. First, because of discrete changes in the basis set at each **k** point as V changes, there is scatter in the calculated $E(V)$ points, the amplitude of which depends both on the energy cutoffs and the **k**-point set. Secondly, the given comparisons include only volumes in the narrow range $168a_B^3-180a_B^3$, since for smaller volumes the bands cross near L, a point included in the 6^3–**k**-point set, and the crossing at this volume is probably an artifact of the LDA band-gap underestimate. Thus the set-A result of 0.51 Mbar is the most reliable, and direct comparison with the calculated energies in sets B and C given in Fig. 2, with allowance for the larger scatter in these sets, indicates that the convergence should be considered acceptable.

The general features of the calculated band structure at $V_{\min}=169a_B^3$, shown in Fig. 3, compare well with previous empirical-pseudopotential-method calculations.[14–16] We see that rocksalt GeTe is a narrow-band-gap-semiconductor with the gap at $L=0.04$ eV, spin-orbit splitting of the upper valence bands at Γ of 0.78 eV, and a secondary maximum or saddle point along $\Gamma-K$ at $0.3(2\pi/a_0)(1,\frac{1}{4},-\frac{1}{4})$, 0.25 eV below the valence-band maximum at L. Unfortunately, measurements of the gap in rocksalt GeTe are not currently available, so no direct comparison with experiment is possible. However, our calculated value of 0.04 eV will almost certainly prove to be an underestimate. This is due in part to the generic underestimate of band gaps in density-functional calculations and in part to the use of the energy-minimizing volume rather than the larger experimental value for the volume, for which a calculation of the bands at L gives a gap of 0.12 eV.

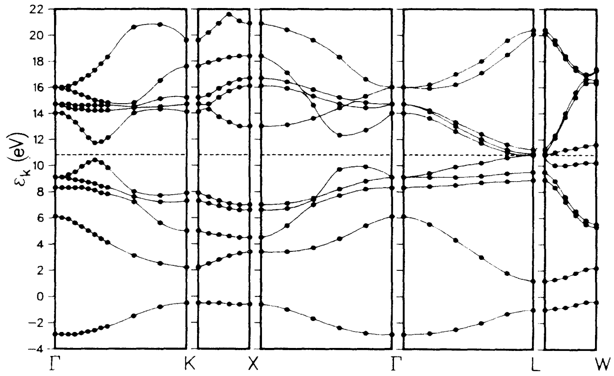

FIG. 3. Pseudopotential band structure of GeTe in the rocksalt structure with atomic volume $169a_B^3$, including spin-orbit coupling. In units of $2\pi/a_0$, $\Gamma=(0,0,0)$, $L=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $W=(1,\frac{1}{2},0)$, $K=(1,\frac{1}{4},-\frac{1}{4})$, and $X=(1,0,0)$. The gap of 0.04 eV at L is too small to be visible on this plot. The energy of the top of the valence band is indicated by a dashed line.

The total scalar-relativistic pseudocharge density, shown in Fig. 4, reflects the mixed ionic-covalent bonding also characteristic of SnTe and PbTe.[1] The charge transfer from Ge to Te is less than that from Pb to Te, indicating that the bonding in GeTe is less ionic, while in GeTe the deviation from spherical symmetry of the Te ion, associated with covalent bonding, is slightly more pronounced than in PbTe.

The difference between GeTe and PbTe is particularly apparent in the band-by-band charge densities shown in Fig. 5. The lowest four bands are similar in the two compounds—the first is Te s-like, the second Ge (Pb) s-like, and the third and fourth are Te p-like. However, the fifth band, which is a mixture of Ge (Pb) p and Te p, has

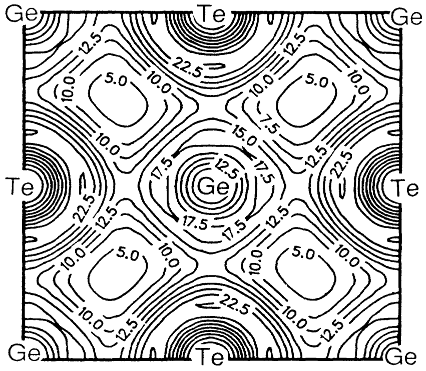

FIG. 4. Total pseudocharge density of rocksalt GeTe with atomic volume $169a_B^3$ in the (100) plane. Densities are given in units of electrons per two-atom unit cell.

TABLE I. Minimum crystal energy, lattice constant, and bulk modulus in the rocksalt structure extracted from quadratic polynomial fits to calculations done with three different sets of energy cutoffs and **k** points, compared to experiment.

Energy cutoffs (Ry)	**k**-point set	Minimum crystal energy (Ry/atom)	Lattice constant (Å)	Bulk modulus (Mbar)
(10.5,16.5)	7^3	−12.228 84	5.85	0.51
(10.5,16.5)	6^3	−12.228 18	5.83	0.41
(11.5,18.0)	6^3	−12.227 34	5.87	0.60
Experiment			6.01(670 K)[a]	

[a] Reference 7.

much more charge associated with the cation in the case of GeTe, while the lowest conduction band, a roughly equal mixture of Pb p and Te s in PbTe, is predominantly Ge p-like in GeTe. The increased involvement of Ge p levels is probably associated with the greater instability of GeTe against the distortions corresponding to the rhombohedral structure, described below.

IV. RESULTS: RHOMBOHEDRAL STRUCTURE

The observed low-temperature structure of GeTe can be considered as a distortion of the rocksalt structure by the relative displacement of the two fcc sublattices by $a_0\tau(111)$ and a subsequent rhombohedral shear along (111) which changes the rhombohedral angle from its fcc value of 60° to α (Fig. 6). The first question we address is the stability of the rocksalt structure against this distortion. First, we vary τ, holding α at 60° and volume at the rocksalt-structure energy minimum 169 a.u. (Fig. 7). We see that the energy gain from this distortion alone is significant. Since this distortion energy is particularly sensitive to **k**-point convergence, we show the calculations explicitly for three sets of increasing size ($6^3=196$, $7^3=343$, and $9^3=729$) with energy cutoffs (10.5,16.5 Ry).

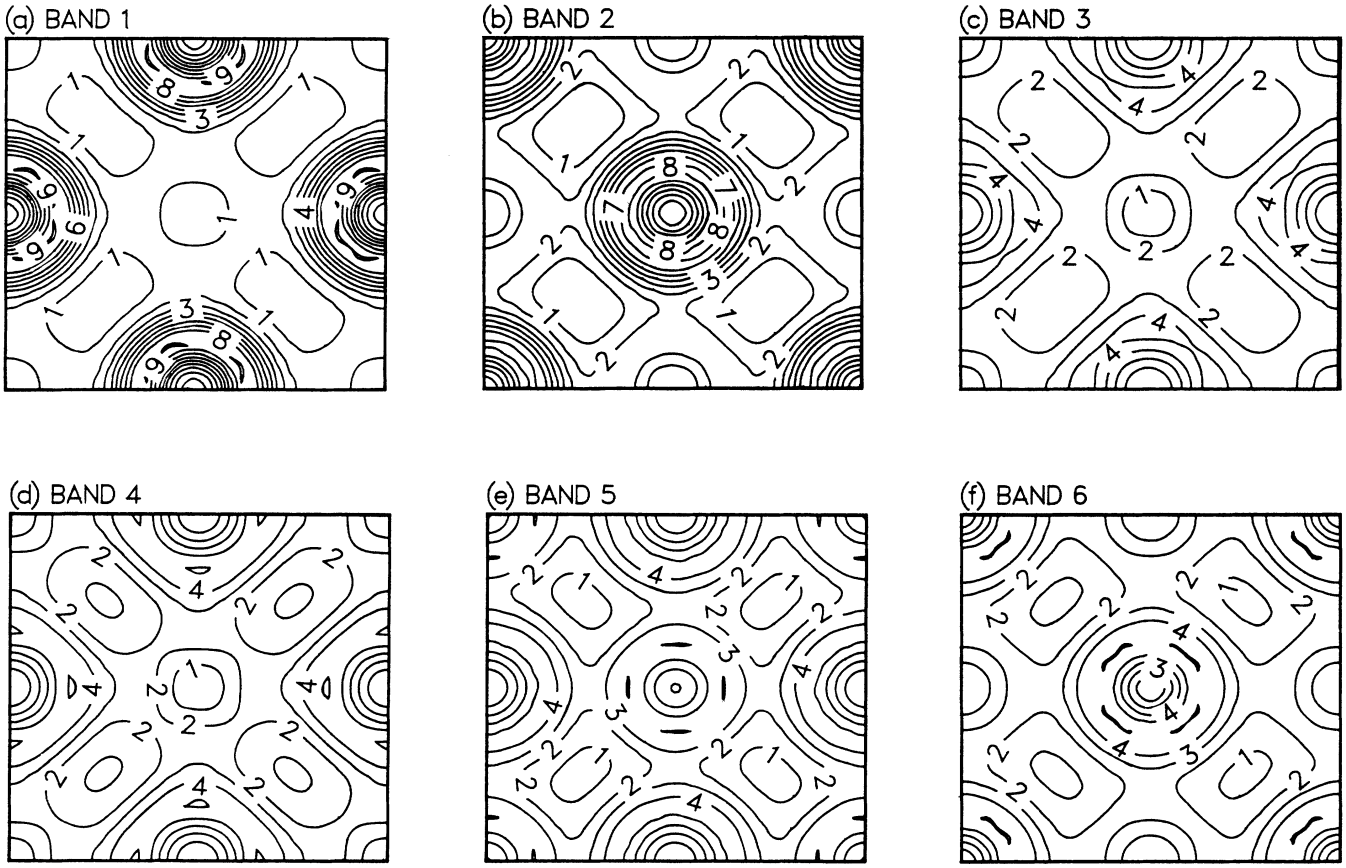

FIG. 5. Band-by-band pseudocharge densities of rocksalt GeTe in the (100) plane for bands 1–6, (a)–(e), respectively, in units of electrons per unit cell. Positions of Ge and Te atoms are the same as in Fig. 4.

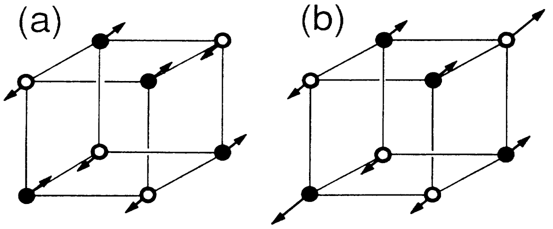

FIG. 6. Rhombohedral structure of GeTe is obtained from the rocksalt structure by a two-step distortion: (a) relative displacement of the two fcc sublattices by $a_0\tau(111)$, and (b) rhombohedral shear along (111).

In a polynomial fit to $E(\tau)$, the quadratic coefficient is converged to about 10%. On the other hand, energy convergence is extremely good. Calculations with cutoffs of (11.5,18.0 Ry) and 6^3 **k** points (set C of Table I) coincide with points calculated with the lower energy cutoff on the scale of the figure, with the deviation increasing with τ to a maximum of 1 meV at $\tau=0.04$.

Next we vary α with $\tau=0$ and $V=169$ a.u. (Fig. 8). The rocksalt structure is seen to be stable against rhombohedral shear, and we obtain a value for the shear elastic constant of the rocksalt structure, $C_{44}=1.8\times10^{11}$ dyn/cm^2. Since there is no experimental measurement of C_{44} for GeTe, we compare the calculation to the SnTe value $C_{44}=1.4\times10^{11}$ dyn/cm^2,[17] finding reasonable agreement. We demonstrate convergence in **k**-point-set and basis-set size by including the results of other calculations (sets B and C of Table I) in the figure. Again, because the shape of the unit cell is changing, we see some scatter in the points which, as in the rocksalt structure, is especially noticeable for set B. Otherwise, the convergence appears to be good, with C_{44} converged to about 10%.

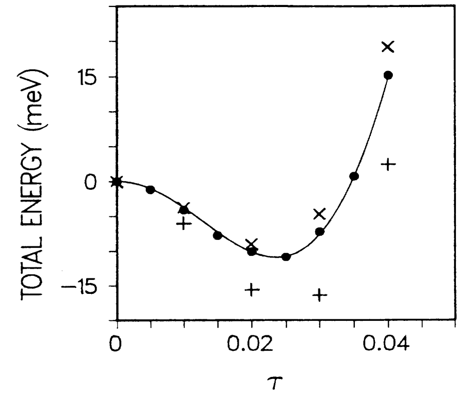

FIG. 7. Total energy in meV/atom of GeTe as a function of τ with α fixed at 60°. The solid circles are points calculated with 7^3 **k** points, vertical crosses with 6^3 **k** points and diagonal crosses with 9^3 **k** points. The fit to the points calculated with 7^3 **k** points to a polynomial quartic in τ^2 is shown as a solid line. For each set, the calculated value at $\tau=0$ is selected as the zero of energy.

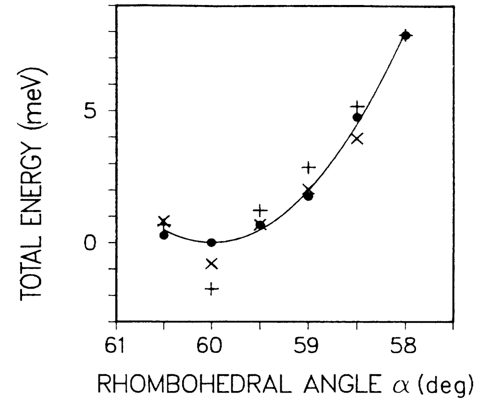

FIG. 8. Total energy in meV/atom of GeTe as a function of α with $\tau=0$. The solid circles are points calculated with set A cutoffs, vertical crosses with set B, and diagonal crosses with set C (see Table I). The solid line is a parabolic fit to the points in set A. For each set, the minimum of a parabolic fit is selected as the zero of energy.

Finally, we study a range of values of τ and α to determine the zero-temperature equilibrium lattice parameters. The results are fit to within 10^{-4} Ry and the fit is shown in Fig. 9 as a contour plot. The resulting lattice parameters are $\alpha=58.8°$ and $\tau=0.025$, to be compared with the experimental values (57.9°,0.026) (Ref. 18) and (58.0°,0.034) (Ref. 8).

The band structure at the minimum-energy configuration is shown in Fig. 10. Because inversion symmetry is slightly broken, the bands are spin split. For this distortion, we find a gap at L of 0.4 eV, with a secondary valence-band maximum 0.18 eV lower at T, and another maximum or saddle point 0.27 eV lower along Γ-K. Tunneling spectroscopy gives a value of 0.1–0.2 eV for the fundamental gap.[19] Since the gaps at L and T and the existence of an indirect gap are quite sensitive to the distortion, our overestimate of the gap

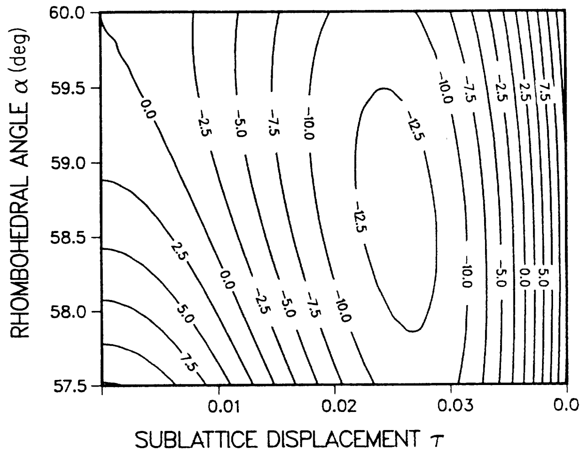

FIG. 9. Contour plot of the fit to $\Delta E_{\mathrm{tot}}(\alpha,\tau)=E_{\mathrm{tot}}(\alpha,\tau)-E_{\mathrm{tot}}(\alpha=60°,\tau=0)$. Energies shown are in meV/atom.

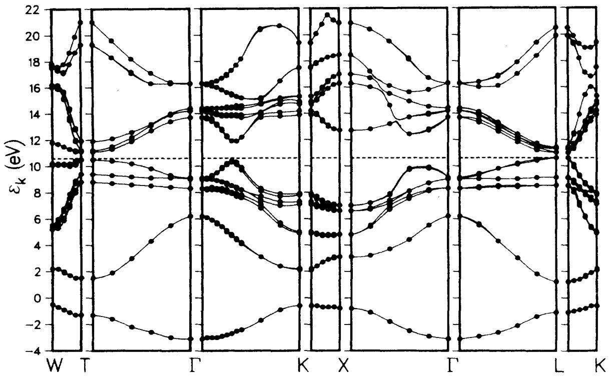

FIG. 10. Pseudopotential band structure of GeTe in the rhombohedral structure with atomic volume $169a_B^3$ and distortions $\alpha=58.8°$ and $\tau=0.025$, including spin-orbit coupling. In units of $2\pi/a_0$, $\Gamma=(0,0,0)$, $T=(\frac{1}{2},\frac{1}{2},-\frac{1}{2})$, $L=(\frac{1}{2},\frac{1}{2},-\frac{1}{2})$, $W=(1,\frac{1}{2},0)$, $K=(1,\frac{1}{4},-\frac{1}{4})$, and $X=(1,0,0)$. The energy of the top of the valence band is indicated by a dashed line.

might be accounted for by the difference between the structural parameters of the calculated minimum-energy configuration and those of the thin polycrystalline films in which the tunneling experiments were performed.

We have studied the trends in band edges at L and T with distortion in more detail. For $\alpha=60°$, as τ increases, the conduction-band minima increase and the valence-band maximum at L decreases slightly, while the valence-band maximum at T decreases strongly. For $\tau=0$, as α decreases, the gaps at L and T increase slightly and the levels at L drop while those at T rise, keeping the weighted average constant. Fitting the results for varying α to a straight line, we can obtain the shear deformation-potential constant, defined as $\Xi=(\sqrt{3}/2)(\Delta/\phi)$, where Δ is the L-T energy splitting and ϕ is the deviation of α from $2\pi/3$. Our calculated value $\Xi=10$ eV is comparable to $\Xi=5-7$ eV derived from measurements of the anisotropy of the resistivity below T_c.[20,21]

V. DISCUSSION

The lack of complete experimental data on the elastic constants and band structure of GeTe is partly a consequence of the intrinsic limitations on the quality of samples and, for rocksalt GeTe, the high temperature at which the form exists. These limitations arise because the range of homogeneity of the alloy does not include the stoichiometric composition, but lies on the Te-rich side.[22-24] The Ge vacancies and other lattice defects, in addition to possibly modifying the structural properties of the material directly, give rise to a large concentration of free holes. In fact, tunneling spectroscopy shows that ϵ_f lies 0.4–0.5 eV below the top of the valence band,[19] and Hall measurements[25] typically show $p \sim 10^{20}-10^{21}$ cm^{-3}.

The effects of nonstoichiometry can be important in the comparison of experimental and calculated quantities. For example, in going from the rocksalt to the rhombohedral structure, there is an energy gain from the redistribution of holes among the L and T maxima, called the "intervalley Jahn-Teller effect.[26] The lowering of C_{44} for typical hole concentrations is measured in SnTe to be as large as 35%,[17] and is expected to be important in GeTe as well.

Aside from the use of finite basis and **k**-point sets, the most important approximations in the calculation are the pseudopotential and local-density approximations. As mentioned earlier, the use of the LDA overestimates the cohesive energy of GeTe due to the inaccuracy in the calculation of the free-atom energy. Moreover, since density-functional theory underestimates the gaps in semiconductors, we fill the five lowest bands completely, even when the gap is slightly negative. This occurs for small volumes in the rocksalt structure or for the rhombohedral structure when τ is 0 and α is not equal to 60°. By the same token, it is reasonable, even when we use this method to study finite-temperature properties, to keep the electrons at zero temperature despite the fact that our calculated gap for the rocksalt structure is less than kT_c. Finally, as is known from experience in a variety of systems,[27] this method underestimates the lattice constant. Though this underestimate is not in itself very significant, when we determine the structural parameters of the rhombohedral form, the errors in the calculation of the distortion energy are convoluted with the volume error. Since a decrease in volume should favor the more symmetric rocksalt structure and dT_c/dP is observed to be negative, the result is that for all three materials, GeTe, SnTe, and PbTe, the stability of the rocksalt structure is greater than that inferred from experiment.

In summary, we have calculated and studied the convergence of lattice parameters, elastic constants, and band structures of the rocksalt and rhombohedral forms of GeTe, and obtained good agreement with experimental measurements, when available. We conclude that the *ab initio* scalar relativistic pseudopotential total-energy method can be used to provide an accurate description of the structural properties of GeTe.

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