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High-temperature electron-band calculations*

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Self-consistent electron-band theories have by now succeeded in producing rather impressive agreement with experiment for the low-temperature low-pressure bulk properties of metals. An abundance of high-temperature high-pressure shock-compression data offers an excellent proving ground for extension and testing of these methods under more extreme conditions. One important problem in such an application is a treatment of the electronic excitations. This is the concern of the present paper. Finite-temperature self-consistent electron-band calculations were performed for temperatures up to 22000 K, using the test case of compressed metallic iodine. Electron-phonon coupling was neglected, and the structure assumed to be a rigid face-centered-cubic lattice. Results for the finite-temperature total electronic energy and pressure obtained by the fully self-consistent calculations were found to be in close agreement with model calculations based solely on the ground-state electronic density of states and Fermi-Dirac statistics. This suggests the possibility of the significant savings in computational effort for high-temperature equation-of-state band calculations suitable for comparison with shock-compression data.

I. INTRODUCTION

This paper reports *high-temperature* (up to 22000-K) *self-consistent*-augmented-plane-wave-$X\alpha$ (SC-APW-$X\alpha$) calculations for the test case of compressed face-centered-cubic (fcc) metallic iodine. By comparison to these results, a simple model calculation of the total electronic energy and pressure based only on ground-state properties is shown to be surprisingly accurate even up to these temperatures. The reason for such an unusual choice of materials for an exploratory calculation revolves around the practical need to interpret what appeared to be some highly perplexing experimental data on molecular iodine that had been shock compressed to 110 GPa (1.1 Mbar) and 20000 K.[1] The need to distinguish between the properties of the monatomic metal and the molecular crystal while attempting to understand this data motivated our use of these techniques. The actual comparisons of theory with experiments on iodine and the nuances that such comparisons inevitably excite are discussed in the paper following.[2] Here we confine our attention to the details of the finite-temperature electron calculations, which although applied to iodine, are quite as general and applicable as the augmented-plane-wave (APW) method itself.

At the present time first-principles calculations of the pressure and energy of metals at 0 K can be carried out by a relatively straightforward application of self-consistent electron-band theory, principally by the APW and the equivalent Korringa-Kohn-Rostoker methods. These methods and their applications are by now well documented.[3,4] They employ local free-electron approximations to the exact exchange-correlation expressions that result in enormous computational simplification without significantly comprising the final results. The only serious debate is the question of the most appropriate approximation. In the so-called $X\alpha$ method,[5] what is essentially a free-electron expression for just the exchange energy appears multiplied by an adjustable parameter α. Different theoretical recipes for α provide the user with crystal potentials, which, in fact, differ little. A more unambiguous approach without adjustable parameters is provided by Hedin and Lundqvist.[6] This approximation is based on free-electron expressions for both the exchange and correlation effects, although again the crystal potential differs little from that of the $X\alpha$ method; and the choice would appear to be one of taste and convenience. While it is tempting to argue that the latter method is more appropriate since it is based on theory and contains no adjustable parameters, any free-electron approximation to exchange and correlation effects is of questionable reliability in the case of rapidly varying electron density as occurs in condensed matter and atoms.[7] In spite of this uncertainty, a variety of self-consistent APW and Korringa-Kohn-Rostoker calculations, using both the $X\alpha$ and Hedin-Lundqvist approximations, have produced rather dramatic agreement with experiment for cohesive energies, equilibrium lattice constants, and isothermal compressibilities.[8-17] The calculations of Moruzzi *et al.* for the 3*d*- and 4*d*-series metals should be noted in particular.[18]

In broad overview, the understanding of theoretical and computational methods required for reliable low-pressure low-temperature equation-of-state calculations on metals is already available. A next logical step is the extension and testing of these methods under more extreme conditions of pressure and temperature. There have already been a few comparisons of 0-K theory with static high-pressure measurements of room-temperature isotherms.[13,19] (The correction between 0-K and room-temperature isotherms can in general be reliably managed.) Unfortunately, there are only limited static high-pressure-versus-density results available above 10 GPa or so. Most static work at higher pressures is on resistivity versus pressure. In contrast, there are by now abundant pressure-versus-density data on a variety of materials from shock-compression experiments.[20] Such experiments commonly achieve pressures up to a few megabars (200 GPa), but with concomitant heating of the sample to high temperatures.

In the case of alkali metals, the traditional testing ground of solid-state theory, temperatures can be as high as a few eV (20 000 K). The shock data must then be reduced to 0 K. Since a complete theory of the thermal equation of state of metallic solids is not available, the interpretations of the data have had to resort to rather crude phenomenological theories. An example of the resulting ambiguity is well demonstrated in the work of Grover *et al.*,[21] where it is shown that the reduction procedures commonly followed by different shock-wave groups may result in very different 0-K isotherms for the alkali metals. As a rule the high-temperature theory of matter used to reduce the shock data to 0 K is less good than the 0-K calculation, which is presumably to be compared with experiment. In the case of materials such as the transition metals, temperature rises are modest and the reduction procedures may be adequate. In general, however, the theorist who compares his calculations with reduced shock data will often be undertaking a questionable exercise. An important point we wish to make here is that the theorist who desires to compare his high-pressure calculations to the primary experimental data may have no choice but to pursue his calculations to higher temperatures.

Any theory of metals must account for the properties of both the electronic and the nuclear degrees of freedom. This effort is complicated by the electron-phonon coupling, and by the loss of crystal symmetry if temperatures are above melting. In attempting to formulate a first-approximate theory, the appropriate treatment will depend on the particular density and temperature range of interest. Thus, for example, the 0-K treatments described earlier assume that electron-phonon coupling is negligible, and, of course, have no concern with liquid disorder. In this approximation the electronic properties are calculated, assuming a rigid lattice of nuclei. Small corrections for the zero-point motion of the nuclei are obtained from simple harmonic models and added to these results to obtain the total energy and pressure of the solid.

What about shock-wave data? For temperatures extending into the electron-volt range, it is immediately clear that special attention must be paid to a treatment of the electronic degrees of freedom that explicitly incorporates electronic excitations. From the point of view of computational ease, however, one hopes it may still be possible in a first-approximate treatment to use a rigid-lattice calculation for the electrons in conjunction with, say, a harmoniclike Grüneisen model for the lattice thermal motion. In spite of the very high temperatures involved, such an approximation is, in fact, not totally unreasonable. It should be emphasized that the high temperatures in shock compression occur simultaneously with much increased density, and thus the ratio of temperature to melting temperature may only get as high as a factor of 5 or so. It is this ratio that is important to these approximations. At least for temperatures somewhat higher than melting, Stroud and Ashcroft[22] have indeed found that the free energy of normal-density crystalline sodium can be well approximated by such a rigid-lattice band-structure calculation combined with a pseudoharmonic treatment of the nuclear motion. Furthermore, the rather weak temperature dependence of their pseudoharmonic Debye temperature suggests that even the further approximate Grüneisen model might suffice for the nuclear motion.

There is somewhat more evidence that neglect of liquid disorder is a reasonable first approximation in a theoretical calculation of shock-compression curves. It is, of course, intuitively clear that at any given instant the local environment experienced by an atom in a liquid is about the same as in a solid. In fact, both the solidlike Lennard-Jones–Devonshire cell model and liquid-perturbation theory predict results for the shock-compression P-V curve of initially solid argon that are in reasonable agreement (i.e., within experimental error) up to temperatures fully a factor of 4 larger than the melting temperature.[23] Furthermore, it is generally not possible to distinguish where melting has occurred by inspection of the experimental shock-compression data.[24]

The preceding discussion was intended to motivate a practical approach for a theoretical treatment of high-temperature high-density metals suitable for comparison with shock data. As a first approximation we propose to separate the nuclear and electronic degrees of freedom, using self-consistent band theory for the high-temperature electronic degrees of freedom (assuming a rigid lattice of nuclei), and treating the thermal nuclear motion separately by means of a Grüneisen model. To date considerable effort has been expended in treating the thermal motion of metals; however, the high-temperature, electronic problem has received little attention and is the sole concern of the present paper.

The organization of this paper is as follows. In Sec. II we review the SC-APW-$X\alpha$ method and calculations with specific attention to its finite-temperature form. Finite-temperature SC-APW-$X\alpha$ calculations were carried out at five temperatures up to 22 000 K, all at a single density. In Sec. III we introduce an approximate model for computing thermal energy and pressure based only on the ground-state density of states and Fermi-Dirac statistics. Results of these model calculations are compared with the above finite-temperature SC-APW-$X\alpha$ calculations, and are in excellent agreement up to the highest temperatures considered (22 000 K). We present our summary in Sec. IV.

II. SELF-CONSISTENT AUGMENTED-PLANE-WAVE $X\alpha$ METHOD

The zero- and finite-temperature electronic properties of fcc monatomic iodine were calculated by means of the SC-APW-$X\alpha$ method in the non-spin-polarized and nonrelativistic form.[4] In its customary ground-state form, this method may be simply viewed in terms of the variational minimization of a particular approximate expression for the total energy.[25] Since the variational point of view is a well-established principle of statistical thermodynamics, it permits a straightforward generalization of the derivation to finite temperatures, carried out by applying this principle to the minimization of the Helmholtz free energy.

A. Zero-temperature theory

Consider the following expression for the total energy of a system of NZ electrons within a rigid lattice of N nuclei:

$$E=\sum_i n_i \int d^3r\, u_i^*(\vec{r})(-\nabla^2)u_i(\vec{r}) -\sum_a \int d^3r\, \frac{2Z\rho_{\mathrm{MT}}(r)}{|\vec{r}-\vec{R}_a|} +\frac{1}{2}\int d^3r\, d^3r'\, \frac{2\rho_{\mathrm{MT}}(\vec{r})\rho_{\mathrm{MT}}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} +\tfrac{3}{4}C_\alpha \int d^3r\, \rho_{\mathrm{MT}}(\vec{r})^{4/3}+\sum_{a<b}\frac{2Z^2}{|\vec{R}_a-\vec{R}_b|}\ . \tag{1}$$

The index i runs over orthonormal spin orbitals $u_i(\vec{r})$; the index a runs over the lattice sites. Atomic units are used throughout this paper.[26] The constant $C_\alpha=-3\alpha(3/\pi)^{1/3}$. For the time being we shall be concerned with zero temperature, in which case the occupation numbers n_i are either zero or unity and serve to restrict the sum over i to occupied spin orbitals.

Equation (1) may be recognized as the Hartree-Fock expression for the total energy with two approximations: (i) The correct nonlocal-exchange interaction is replaced by Slater's $\rho^{1/3}$ approximation multiplied by an adjustable parameter α (thus, the name $X\alpha$). There are well-prescribed methods for choosing α that generally indicate $\alpha\simeq 0.7$ for all but the lightest elements.[27,28] It has been argued that some correlation energy is included in this method, and that it may yield a better approximation to the correct many-body energy than does the Hartree-Fock approach.[5] (ii) In the potential energy terms the correct charge density

$$\rho(\vec{r})=\sum_i n_i\, |u_i(\vec{r})|^2 \tag{2}$$

is replaced by its muffin-tin approximation. Inscribe contiguous muffin-tin spheres of equal size about each lattice site. The muffin-tin approximation to a function $f(\vec{r})$, designated by $f_{\mathrm{MT}}(\vec{r})$, is taken to be the spherical average of $f(\vec{r})$ within these spheres, and a constant in the interstitial region equal to the average value of $f(\vec{r})$ within that same interstitial region. The muffin-tin approximation is believed to be quite good for close-packed monatomic metals in which a relatively small fraction of the electron density exists outside of the muffin-tin spheres. The approximation is considered less reliable for more open-lattice structures and also where any significant component of covalent bonding introduces strong orientational dependence into the electron density.[4]

In spite of the muffin-tin approximation, Eq. (1) is a well-defined functional of the spin orbitals. The SC-APW-$X\alpha$ method serves rigorously to minimize Eq. (1) with respect to these orbitals. The resultant differential equation for the orbital u_i and its energy ϵ_i may be written

$$[-\nabla^2+W_{\mathrm{MT}}(\{\rho_{\mathrm{MT}}\},\vec{r})+C_\alpha\rho_{\mathrm{MT}}(\vec{r})^{1/3}]u_i(\vec{r}) =\epsilon_i u_i(\vec{r})\ , \tag{3}$$

where

$$W(\{\rho\},\vec{r})=\sum_a \frac{-2Z}{|\vec{r}-\vec{R}_a|}+\int d^3r'\, \frac{2\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\ . \tag{4}$$

The total energy in the SC-APW-$X\alpha$ method is given by Eq. (1), evaluated with the optimized orbitals. Since the potential energy terms all scale as $V^{-1/3}$, a direct consequence of the variational minimization is that the SC-APW-$X\alpha$ kinetic energy [first term in Eq. (1)] and potential energy (remaining terms) must satisfy the virial theorem

$$PV=\tfrac{2}{3}E_{\text{kin}}+\tfrac{1}{3}E_{\text{pot}}, \qquad (5)$$

when these expressions are evaluated with the optimized orbitals.[29]

B. Finite-temperature theory

We turn to the finite-temperature version of the theory. Following an approach used by Slater,[5] we consider the Helmholtz free energy

$$F=E+k_BT\sum_i\left[n_i\ln n_i+(1-n_i)\ln(1-n_i)\right], \qquad (6)$$

where E is as in Eq. (1), and the entropy is that appropriate to a Fermi gas. The sum over i runs over *all* the energy levels. Equation (6) is now to be minimized with respect to both the spin orbitals and the occupation numbers, subject to the constraint $\sum n_i=NZ$. The variational principle leads to Eq. (3) as before, but now the orbital-occupation numbers are represented by the Fermi-Dirac distribution function as to be expected

$$n_i=\{\exp[\beta(\epsilon_i-\mu)]+1\}^{-1}. \qquad (7)$$

The chemical potential μ is, of course, fixed by the constraint on the sum over n_i. Because of Eq. (7), the self-consistent charge density and the self-consistent potential in Eq. (3) are temperature dependent. Note that the virial theorem, Eq. (5), still follows from the finite-temperature derivation.

The major uncertainty in the finite-temperature SC-APW-$X\alpha$ method is the suitability of the local-exchange approximation. We have admittedly taken the simplest logical generalization of the zero-temperature form, the same $\rho^{1/3}$, although with the local charge density now temperature dependent. However, we emphasize that this approximation is only to be used within the region of electron degeneracy, $T/T_F\leq 0.2$. In the case of shock compression, this criterion may often be satisfied even at electron-volt temperatures. These high temperatures occur simultaneously with much increased density, so that the Fermi temperature is also much larger both because the volume is substantially decreased and because more electrons are pressure ionized.

C. Calculations

A series of zero-temperature SC-APW-$X\alpha$ calculations were performed at a number of densities. Finite-temperature SC-APW-$X\alpha$ calculations were performed at one density. The value of α was taken to be 0.7001, chosen so that the energy for the isolated atom as calculated with the $X\alpha$ approximation would equal the isolated-atom Hartree-Fock energy.[30] It is to be emphasized that all electrons are included and treated self-consistently, although the localized core electrons are treated in a self-consistent atomic fashion. At zero temperature, monatomic crystalline iodine has a $\frac{5}{6}$-filled $5p$ band. The $5s$, $5p$, and higher states were treated in the band mode, using the equivalent of 256 points in the full Brillouin zone. This number was judged to be adequate when a calculation with 2048 points yielded a total energy different by only 0.003 Ry and a pressure different by only a few kbar. The radial mesh was of the Herman-Skillman[31] doubling form, with 225 points out to the muffin-tin sphere.[32] Sums over angular momentum were truncated after 13 values. Running time on the CDC-7600 was about 1 min/iteration for the ground-state calculations (about 2 min at $T=22\,000$ K), and generally ten iterations were required for convergence of the total energy and pressure to about ±0.0005 Ry and ±0.5 kbar, respectively.

The density selected for the finite-temperature SC-APW-$X\alpha$ calculations corresponds to a relative volume $V/V_0=0.4738$, where V_0 is the volume *per atom* of normal-density diatomic molecular iodine ($V_0=25.674$ cm^3/mole I).[33] Five temperatures were taken ranging from 0 to 22 000 K. These choices are compatible with conditions actually encountered in shock compression of iodine. Furthermore, in shock compression to the above volume, the temperature achieved would be sufficient (presuming a monatomic phase) to have excited a significant number of electrons into the previously empty $5d$ band, lying just above the $5p$-valence band. The relation between these bands (at $T=0$, [100] direction) is illustrated in Fig. 1. Our exploratory calculations, thus, not only have some relevance to experimental data, but also offer a more interesting test of the effects of temperature in the excitation of electrons across a band gap.

The finite-temperature SC-APW-$X\alpha$ calculations included excited states up to at least $7k_BT$ above the chemical potential for each of the temperatures considered. The chemical potential was never more than 0.04 Ry larger than the Fermi energy. It is to be emphasized that the local charge density was computed by summing over *all* of these states up to the cutoff, weighted, of course, by the Fermi-Dirac distribution function. This spatial and temperature-dependent charge density was used to compute a new tem-

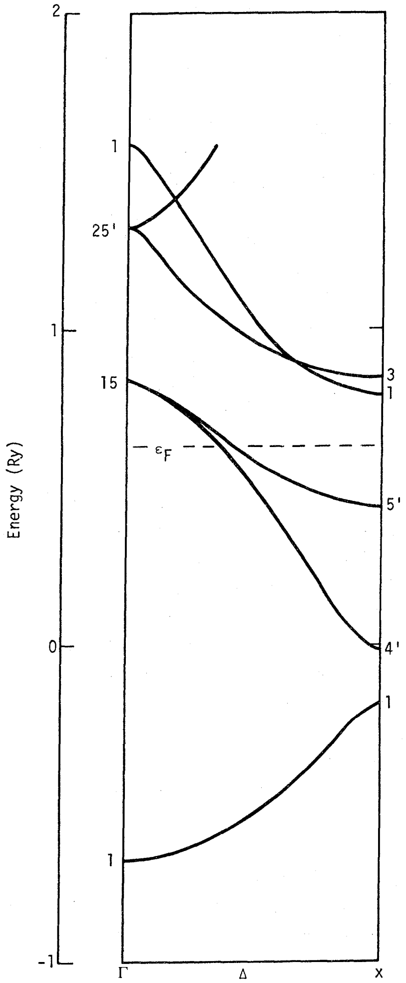

FIG. 1. Band structure of fcc monatomic iodine. The $T=0$ band structure is given in the [100] direction for a relative volume of $V/V_0=0.4738$. The 5*s*, 5*p*, and part of the 5*d*-6*s* bands are shown. The Fermi energy (ϵ_F) is given by the dashed line. All energies are measured relative to the constant potential outside of the muffin-tin sphere.

perature-dependent one-electron potential and the whole process iterated to convergence. It was not necessary to take into account temperature dependence of the occupation numbers for the core electrons. At $T=22\,000$ K, there was essentially no excitation from even the lowest (5*s*) band.

Our results for the electron thermal energy and pressure are presented in Figs. 2 and 3. These thermal properties were obtained at four nonzero temperatures as the differences between results of finite- and zero-temperature SC-APW-$X\alpha$ calculations, given by

$$\Delta E_e(V,T)=E(V,T)-E(V,0)\ ,$$

$$\Delta P_e(V,T)=P(V,T)-P(V,0)\ .$$

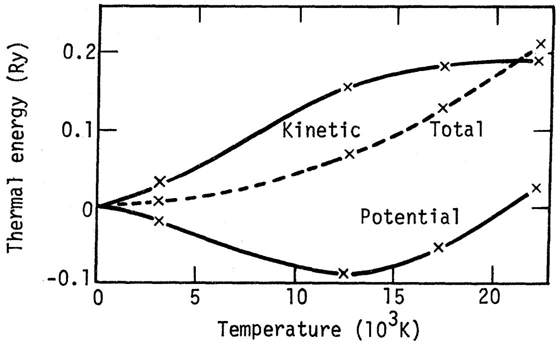

FIG. 2. Thermal energy, $[E(V,T)-E(V,0)]/N$, of fcc monatomic iodine at $V/V_0=0.4738$. The data points were obtained as the difference between finite- and zero-temperature SC-APW-$X\alpha$ calculations. The dashed curve is the result of Eq. (10). Close agreement between the model calculations and the SC-APW-$X\alpha$ calculations is evident. A separation of the total thermal energy into kinetic and potential energies is shown. The change in behavior of these curves for temperatures larger than about 12 600 K is due to the onset of thermal excitations into the 5*d* band.

The pressures were obtained from the viral theorem.

The apparent simple temperature dependence of both energy and pressure hides some interesting structure as can be seen in Fig. 2 in a separation of the finite-temperature SC-APW-$X\alpha$ energy into kinetic and potential contributions. The change in behavior of both curves at a temperature of about 12 600 K is a result of the beginning of thermal excitations into the 5*d* band. This phenomenon is evident in the self-consistent charge density also. Up to temperatures of about 12 600 K the different

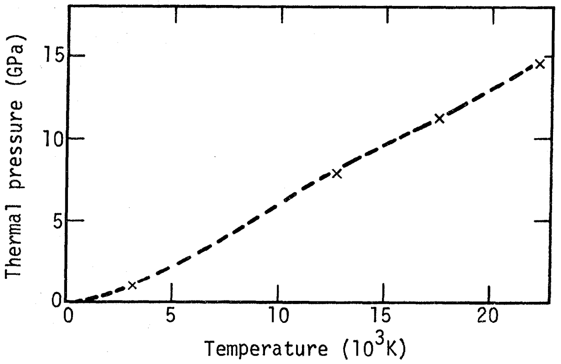

FIG. 3. Thermal pressure, $P(V,T)-P(V,0)$, of fcc monatomic iodine at $V/V_0=0.4738$. The data points were obtained as the difference between finite- and zero-temperature SC-APW-$X\alpha$ calculations. The dashed curve is the result of Eq. (11). Close agreement between the model calculations and the SC-APW-$X\alpha$ calculations is evident.

angular-momentum components of the charge density interior to the muffin-tin sphere stay nearly constant. Between 12 600 and 22 000 K, however, the amount of p-character charge density decreased by about 3% with the loss being made up largely in increased d character and to a lesser extent with an extension of more charge outside of the sphere. These changes are on the whole rather small. Even at $T=22\,000$ K, the self-consistent charge density is nowhere different by more than $\frac{1}{2}$% from its $T=0$ form.

The finite-temperature SC-APW-$X\alpha$ calculations also show a distinct temperature dependence of the eigenvalues. The dominant effect is first an upward shift in their energies, reaching a maximum at about 12 600 K. With subsequent onset of thermal excitation into the $5d$ band, the eigenvalues begin to decrease and continue to do so up to the highest temperature considered, where they are coincidentally about the same as they were at zero temperature. At $T=12\,600$ K the shifts range from about 0.008 Ry for the inner-core eigenvalues to about 0.002 Ry for the valence-band levels. These seemingly small shifts add up to 0.32-Ry contribution to the total energy at this temperature. This is a large number as may be judged from the energy scale in Fig. 2.

III. MODEL CALCULATIONS

To circumvent the need to carry out fully self-consistent finite-temperature calculations at all the temperatures and densities of interest, we describe an approximate method of calculating the finite-temperature electronic energy and pressure that requires only input from ground-state self-consistent band-structure calculations. It is to be recalled that we have restricted ourselves in this paper to calculating the energy and pressure for a system of electrons moving within a static lattice. For the purposes of the present approximation, we subdivide these quantities into ground-state and thermal contributions

$$E(V,T)=E_0(V)+\Delta E_e(V,T)\ , \tag{8a}$$

$$P(V,T)=P_0(V)+\Delta P_e(V,T)\ . \tag{8b}$$

We shall take $E_0(V)$ and $P_0(V)$ to be the results of zero-temperature SC-APW-$X\alpha$ calculations. The approximation to which we refer has been an obvious choice to many and makes use of the zero-temperature SC-APW-$X\alpha$ electronic density of states and Fermi-Dirac statistics in order to calculate the electronic thermal parts $\Delta E_e(V,T)$ and $\Delta P_e(V,T)$.

It is rigorously the case that a variation of the ground-state electronic energy given by Eq. (1) with respect to the occupation numbers yields

$$dE=\sum_i \epsilon_i\,dn_i\ . \tag{9}$$

This expression is, in fact, obtained for any choice of the exchange or exchange-correlation energy, which may be expressed in terms of the local charge density. It does not obtain from the rigorous Hartree-Fock energy expression, as has been emphasized by Slater.[5] Given Eq. (9), a very natural approximation for the electronic thermal energy is

$$\Delta E_e(V,T)=\sum_i \epsilon_i(V)[n_i(T)-n_i(0)]\ , \tag{10}$$

where $\epsilon_i(V)$ are the *zero-temperature* SC-APW-$X\alpha$ eigenvalues in Eq. (3), and $n_i(T)$ is the Fermi-Dirac distribution function, Eq. (7). This approximation is rigorously equivalent to a finite-temperature SC-APW-$X\alpha$ calculation in the limit of small electronic excitation, i.e., low temperatures. Differentiating the corresponding Helmholtz free-energy expression, one obtains for the electronic thermal pressure

$$\Delta P_e(V,T)=-\sum_i \frac{d\epsilon_i(V)}{dV}[n_i(T)-n_i(0)]\ . \tag{11}$$

Equations (10) and (11) constitute the approximate or model calculation of the electronic thermal effects.

Much has been made of the fact that the $X\alpha$ eigenvalues do not satisfy the Koopmans theorem.[5] Yet it is stressed that these discussions have applied largely to very energetic optical excitations of essentially a localized and, thus, atomic character. In the case of a transition between two delocalized band states, the charge density in the vicinity of a given atom should change by only $O(1/N)$. For this situation, the difference between the $X\alpha$ eigenvalues is expected to be reasonably close to the change in total energy.[5] This expectation is, of course, less clear for highly excited states that are nevertheless still generated from the ground-state self-consistent potential. In the final analysis, we justify our use of Eqs. (10) and (11) by comparison with results of finite-temperature SC-APW-$X\alpha$ calculations.

To evaluate Eqs. (10) and (11), ground-state SC-APW-$X\alpha$ calculations were performed at a number of densities to determine the eigenvalues $\epsilon_i(V)$ and their volume dependence. In all cases, excellent fits to the volume dependence of the eigenvalues could be obtained using the functional form $a+bV+cV^{-d}$. Equations (10) and (11) were evaluated for $V/V_0=0.4738$, including $5s$, $5p$, and higher states up to a cutoff of $7k_BT$ above the chemical potential. The results for the thermal electronic energy and pressure are shown in Figs. 2 and 3 as the dashed curves. Close agreement between these approximate calculations and the finite-temperature SC-APW-$X\alpha$ results is evident, up to the highest temperature considered (22 000 K).

Equation (10) would be trivially valid if the finite-temperature SC-APW-$X\alpha$ eigenvalues and potential energy terms showed negligible temperature dependence. It is to be emphasized that this is *not* the case here. We have noted in Sec. II that the temperature-dependent shifts in the finite-temperature SC-APW-$X\alpha$ eigenvalues contributed as much as 0.3 Ry to the total energy, a very large number judging from the energy scale in Fig. 2. The evident success of Eq. (10), which is based on zero-temperature eigenvalues, must, therefore, imply that considerable cancellations occur between the temperature-dependent variations in the finite-temperature SC-APW-$X\alpha$ eigenvalues and potential energy terms. We suspect that the reason for this cancellation and for the success of Eq. (10) lies in the variational nature of the ground-state $X\alpha$ eigenvalues, namely, $\delta E/\delta n_i = \epsilon_i$.

IV. SUMMARY

In seeking a first-approximate theory of metals suitable for comparison with high-temperature high-pressure shock data, we have suggested that one might use a rigid-lattice finite-temperature self-consistent band-structure calculation for the electronic degrees of freedom in conjunction with a Grüneisen model for the nuclear-vibrational motion. Such an approach, of course, neglects electron-phonon coupling, anharmonic nuclear-vibrational effects, and liquid corrections. While these approximations must certainly be tested, our concern in this paper has been with the first part of the problem—self-consistent electron-band structure calculations up into the electron-volt range.

We have reported finite-temperature SC-APW-$X\alpha$ calculations up to a temperature of 22 000 K for the test case of compressed-fcc monatomic iodine. Although more time consuming, these calculations are no more complex than the familiar ground-state method. The effect of electronic excitations is discernable in the temperature dependence of the kinetic and potential energies, pressure, self-consistent charge density, and one-electron eigenvalues. The onset of thermal excitations across the $5p$-$5d$ band gap alters the temperature dependence of these quantities. Even at 22 000 K, however, the self-consistent charge density is nowhere more than $\frac{1}{2}\%$ different from its zero-temperature form.

We have compared the finite-temperature SC-APW-$X\alpha$, total energy and pressure with the same quantities as obtained from a simple-model computation that requires as input only results from ground-state SC-APW-$X\alpha$ calculations. The energies and pressures obtained by these two methods were in close agreement up to the highest temperatures considered. It should, therefore, be possible to calculate the shock-compression P-V curve for a metal, according the rough method outlined above, with no significant increase in computational effort over that already expended in the established self-consistent electron-band methods for determining the zero-temperature isotherm.

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