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Citation: J. Chem. Phys. **146**, 014705 (2017); doi: 10.1063/1.4973549 View online: http://dx.doi.org/10.1063/1.4973549 View Table of Contents: http://aip.scitation.org/toc/jcp/146/1 Published by the American Institute of Physics

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# Is sodium a superconductor under high pressure?

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(Received 17 November 2016; accepted 20 December 2016; published online 5 January 2017)

Superconductivity has been predicted or measured for most alkali metals under high pressure, but the computed critical temperature ( $T_c$ ) of sodium (Na) at the face-centered cubic (fcc) phase is vanishingly low. Here we report a thorough, first-principles investigation of superconductivity in Na under pressures up to 260 GPa, where the metal-to-insulator transition occurs. Linear-response calculations and density functional perturbation theory were employed to evaluate phonon distributions and the electron-phonon coupling for bcc, fcc, cI16, and tI19 Na. Our results indicate that the maximum electron-phonon coupling parameter,  $\lambda$ , is 0.5 for the cI16 phase, corresponding to a theoretical peak in the critical temperature at  $T_c \approx 1.2$  K. When pressure decreases or increases from 130 GPa,  $T_c$  drops quickly. This is mainly due to the lack of *p*-*d* hybridization in Na even at 260 GPa. Since current methods based on the Eliashberg and McMillian formalisms tend to overestimate the  $T_c$  (especially the peak values) of alkali metals, we conclude that under high pressure—before the metal-to-insulator transition at 260 GPa—superconductivity in Na is very weak, if it is measurable at all. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4973549]

### I. INTRODUCTION

At ambient pressure alkali metals have simple electronic band structures well described by a nearly free-electron model. As the pressure applied on these systems increases, alkali metals evolve through a series of structural phase transitions from the highly symmetric body-centered cubic (bcc) metallic phase to insulating phases with low symmetries.<sup>1–6</sup> High pressure has been observed, in many cases, to enhance superconductivity. Both experiments<sup>7–12</sup> and first-principles calculations<sup>13–20</sup> have found that lithium (Li), potassium (K), rubidium (Rb), and cesium (Cs) exhibit strengthened electron-phonon coupling in their high-pressure structures leading to observable, pressure-induced superconductivity.

Cs was the first alkali metal found, through experimental measurements, to have a superconducting phase near 12 GPa with a critical temperature,  $T_c$ , of 1.3 K.<sup>7</sup> Li was the first alkali metal predicted to be superconducting at ambient pressure with a  $T_c \leq 1$  K.<sup>21</sup> However, experimental measurements revealed no evidence of superconductivity at temperatures above 4 mK.<sup>22</sup> Jarlborg<sup>13</sup> then considered the bcc and the hexagonal closed pack (hcp) structures of Li, and his calculations showed that at pressure  $P \approx 22$  GPa,  $T_c = 2.4$  K. Christensen and Novikov<sup>14</sup> studied the face-centered cubic (fcc) Li and cl16-Li using the rigid-muffin-tin approximation (RMTA<sup>23</sup>), concluding that for cI16-Li,  $T_c$  could be as high as 60-80 K. Their calculations gained immediate attention from experimentalists,  $^{8-10}$  and the measured maximum  $T_{\rm c}$  was found to be between 14 and 17 K for  $P \approx 30-35$  GPa. Later calculations<sup>15-20</sup> employing more rigorous first-principles methods obtained  $T_{\rm c}$  values in closer agreement with experimental data.

Subsequent theoretical works investigated other alkali metals. Shi and Papaconstantopoulos<sup>17</sup> found that in fcc K, Rb, and Cs,  $T_c$  values were in the range of 5–14 K, 6–8 K, and 2–6 K, respectively. Although no experimental evidence<sup>7,11,12</sup> for superconductivity has been found in the fcc phases of these three alkali metals [note that the measured superconductivity in Cs is associated with the Cs-IV (tetragonal) and Cs-V (*Cmca*) phases<sup>7</sup>], their first-principles predictions for K are in good agreement with Sanna *et al.*<sup>16</sup> and Profeta *et al.*<sup>18</sup> Therefore, further experimental efforts are required to clarify this discrepancy.

In contrast to Li, K, Rb, and Cs, previous first-principles studies<sup>15,17</sup> have asserted that  $T_c \leq 1$  K for fcc-Na. This is consistent with experimental measurements, which found no superconductivity in Na at temperatures above 4 K.<sup>11,12</sup> However, previous theoretical and experimental investigations of Na have only explored its superconductivity up to the fcc structure. Na could become significantly more superconducting under yet higher pressures. As pressure increases, Na is subjected to a series of phase transitions: from bcc to fcc at 65 GPa,<sup>24</sup> to the *cI*16 structure at 103 GPa,<sup>25</sup> and to the *tI*19 (*oP*8) structure at about 125–132 GPa<sup>26,27</sup> before entering an optically transparent *hP4* structure at ~200 GPa.<sup>4,6</sup> Based on trends seen in other alkali metals, the critical temperature of Na could become significantly higher at the metallic *cI*16 and/or *tI*19 phases.

In this work, we studied electron-phonon coupling in four metallic phases of Na (bcc, fcc, cI16, and tI19) employing the linear-response approach and first-principles calculations based on density functional perturbation theory (DFPT).<sup>28–30</sup> The electronic structure, phonon spectrum, and the Eliashberg spectral function ( $\alpha^2 F$ ) were determined at pressures ranging from 0 GPa to 260 GPa, in order to evaluate  $T_c$  as a function of P up to the metal-to-insulator transition point. We will briefly

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0021-9606/2017/146(1)/014705/5/\$30.00

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describe the computational methods and technical details in Sec. II, followed by the results of the phase transitions, electronic and phonon band structures, electron-phonon coupling, and superconductivity. Finally, we will discuss why Na is not likely to possess any detectable superconductivity under high pressures.

#### II. THEORY AND COMPUTATIONAL METHODOLOGY

The phonon-mediated, strong coupling Migdal-Eliashberg theory<sup>31,32</sup> was used to calculate the pressure-induced superconductivity of Na. The implementation in ABINIT<sup>33</sup> is similar to that implemented by Liu and Quong.<sup>34</sup> Specifically, the linewidth of the phonon mode ( $\mathbf{Q}_j$ ) due to electron-phonon coupling is obtained by averaging over the Fermi level,  $\varepsilon_{\rm F}$ , to give

$$\gamma_{\mathbf{Q}_{j}} = 2\pi\omega_{\mathbf{Q}_{j}} \sum_{nm} \int \frac{d^{3}k}{\Omega_{\mathrm{BZ}}} |g_{\mathbf{k},n}^{\mathbf{k}+\mathbf{Q}_{j},m}|^{2} \\ \times \delta(\varepsilon_{\mathbf{k},n} - \varepsilon_{\mathrm{F}})\delta(\varepsilon_{\mathbf{k}+\mathbf{Q}_{j},m} - \varepsilon_{\mathrm{F}}), \qquad (1)$$

where  $\omega$  is the phonon frequency,  $\varepsilon$  is the Kohn-Sham eigenvalues, and  $g_{\mathbf{k},n}^{\mathbf{k}+\mathbf{Q}_j,m}$  is the electron-phonon matrix element, which represents scattering of an electron from one Bloch state  $(\mathbf{k}, n)$  to another Bloch state  $(\mathbf{k} + \mathbf{Q}_j, m)$ , with a phonon of frequency  $\omega_{\mathbf{Q}_j}$ . These matrix elements are obtained through linear-response calculations and can be written as

$$g_{\mathbf{k},n}^{\mathbf{k}+\mathbf{Q}_{j},m} = \sqrt{\frac{\hbar}{2M\omega_{\mathbf{Q}_{j}}}} \langle \psi_{\mathbf{k},n} | \hat{\boldsymbol{\epsilon}}_{\mathbf{Q}_{j}} \cdot \nabla_{\mathbf{R}} V_{\mathrm{sc}} | \psi_{\mathbf{k}+\mathbf{Q}_{j},m} \rangle, \quad (2)$$

where M is the atomic mass,  $\hat{\epsilon}_{\mathbf{Q}_j}$  is the phonon polarization vector, and  $\nabla_{\mathbf{R}} V_{sc}$  is the gradient of the self-consistent potential with respect to atomic displacement.

From the line width,  $\gamma_{\mathbf{Q}_j}$ , several parameters for the Migdal-Eliashberg theory can be determined, including the electron-phonon coupling constant ( $\lambda$ ) and the electron-phonon spectral function ( $\alpha^2 F$ ). The electron-phonon coupling constant for phonon  $\mathbf{Q}_i$  is defined by

$$\lambda_{\mathbf{Q}_j} = \frac{\gamma_{\mathbf{Q}_j}}{\pi \hbar N(\varepsilon_{\mathrm{F}}) \omega_{\mathbf{Q}_j}^2},\tag{3}$$

where  $N(\varepsilon_{\rm F})$  is the electron density of states (DOS) at the Fermi level. The electron-phonon spectral function  $\alpha^2 F(\omega)$  is defined in terms of the phonon linewidth as

$$\alpha^2 F(\omega) = \frac{1}{2\pi N(\varepsilon_{\rm F})} \sum_{\mathbf{Q}_j} \frac{\gamma_{\mathbf{Q}_j}}{\omega_{\mathbf{Q}_j}} \delta(\omega - \omega_{\mathbf{Q}_j}). \tag{4}$$

Then the electron-phonon coupling constant,  $\lambda$ , can be expressed as the first reciprocal moment of the electronphonon spectral function  $\alpha^2 F(\omega)$ ,

$$\lambda = 2 \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega.$$
 (5)

Finally we used the McMillan equation<sup>35</sup> as modified by Allen and Dynes<sup>36</sup> to approximate  $T_c$ ,

$$T_{\rm c} = \frac{\omega_{\rm log}}{1.2} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right],$$
 (6)

where  $\omega_{\log}$  is the logarithmic average of phonon frequencies, and  $\mu^*$  is the Coulomb repulsion parameter. In the weak coupling regime, an empirical value of  $\mu^* \sim 0.1$  is often adopted, and in this study  $\mu^* = 0.13$ .

We have performed first-principles calculations within the framework of density functional theory (DFT) using the pseudopotential-planewave approach implemented in the ABINIT package.<sup>33</sup> The OPIUM program<sup>37</sup> was employed to generate a norm-conserving pseudopotential for Na, with a valence electron configuration of  $2s^2 2p^6 3d^{0.5}$  and a radius cutoff of 1.5 bohrs for the s, p, and d orbitals. We used the generalized gradient approximation parameterized by Perdew, Burke, and Ernzerhof (GGA-PBE<sup>38</sup>) for the exchangecorrelation functional. The planewave energy cutoff of 50 hartree and dense k-point meshes of  $24 \times 24 \times 24$  were used for the fcc and bcc phases to guarantee convergence, while a  $12 \times 12 \times 12$  and a  $8 \times 8 \times 8$  k-mesh were used for the *cI*16 and tl 19 phases, respectively. Our linear-response calculations of the lattice vibrations employed DFPT,  $^{28-30}$  using **q**-point meshes of  $8 \times 8 \times 8$  for the bcc and fcc structures while a  $4 \times 4 \times 4$  mesh was used for the *cI*16 and *tI*19 phases.

#### **III. RESULTS AND DISCUSSION**

We first verified structural phase transitions under pressures as high as 260 GPa, where the metal-to-insulator transition occurs. Then we computed the electronic structures and lattice vibrations under increasing pressures for the four metallic phases of Na. We evaluated electron DOS at the Fermi level  $N(\varepsilon_{\rm F})$ , the logarithmic averaged phonon frequencies  $\omega_{\log}$ , and the electron-phonon coupling constant,  $\lambda$ , based on results obtained through DFT and DFPT calculations. Finally, the critical temperatures  $T_{\rm c}$  were determined using the McMillan equation with the calculated  $\lambda$  and  $\omega_{\log}$  at each pressure.

#### A. Phase transitions

We constrained the structural symmetry of Na to study phase transitions between the four metallic phases (bcc, fcc, cI16, and tI19) under a wide range of pressures. Stable phases were found by calculating the enthalpy, where the lowest enthalpy (H = E + PV) corresponds to the most stable structure under a certain pressure at 0 K. Fig. 1 shows that the bcc to fcc transition occurs at 71 GPa, fcc to cI16 at 130 GPa, and cI16 to tI19 at 152 GPa, which is in excellent agreement with



FIG. 1. Enthalpy with respect to the bcc structure for the fcc, *cl*16, and *tl*19 phases.



FIG. 2. Crystal structures of Na in the (a) cI16 and (b) tI19 phases.

previous calculations  $^{1,2,4,14}$  and consistent with experimental measurements.  $^{4,6,25-27}$ 

Here we focus on investigating superconductivity in Na by considering only these four metallic phases. Ma *et al.* theoretically calculated a metal-to-insulator (tI19 to hP4) transition occurring at 260 GPa, while their optical measurements suggested the transition pressure was closer to 200 GPa.<sup>4</sup> Thus, we computed the electron-phonon coupling in Na up to 260 GPa. The *cI*16 structure [Fig. 2(a)] is cubic, containing 9 atoms in its primitive cell, whereas the *tI*19 phase [Fig. 2(b)] is an incommensurate structure, consisting of host and guest atoms, which can be approximated by incorporating a  $1 \times 1 \times 5$  supercell of the guest lattice into a  $1 \times 1 \times 3$  supercell of the host lattice to create a conventional cell with 116 atoms.<sup>4,6,27</sup>

## B. Electronic and phonon band structures

We computed the electronic band structures and densities of state for the four metallic phases of Na at various increasing pressures, as summarized by Fig. 3. The band structures do not change remarkably at different pressures within each phase. When pressure increases and Na goes through the bcc, fcc, cI16, and tI19 phases, the electron DOS at the Fermi level,  $N(\varepsilon_{\rm F})$ , decreases [Fig. 6(a)]. We also find that the fcc and cI16Na are semimetals, in contrast to "real" metallic bcc and tI19phases.

We note that the Fermi surfaces of *all* four metallic phases remain spherical, as shown in Fig. 4, unlike other alkali



FIG. 3. Electronic band structures and density of states (DOS) in units of number of states/ $(eV/bohr^3)$  for the (a) bcc phase at ambient pressure, (b) the fcc phase at 100 GPa, (c) the *cI*16 phase at 140 GPa, and (d) the *tI*19 phase at 220 GPa.



FIG. 4. Fermi surfaces of Na in the (a) bcc, (b) fcc, (c) cI16, and (d) tI19 phases.

metals (Li, K, Rb, and Cs) whose Fermi surfaces of the fcc phase already show cooper-like necks and develop extended nesting.<sup>16,39,40</sup> It indicates that in bcc, fcc, cI16, and tI19 Na, the nearly free-electron model is still valid, and there are no signs of a  $p \rightarrow d$  transition near the Fermi surface under pressures up to 260 GPa. This is consistent with electronic band structures plotted in Fig. 3, which resemble free electron bands within the empty lattice approximation. In the cI16 phase, the *s-p* hybridization leads to an indirect gap,<sup>27,41</sup> as seen in Fig. 3(c).

Fig. 5 summarizes the calculated phonon band structures and DOS for bcc, fcc, cI16, and tI19 Na. Panel (a) shows that as pressure increases from 0 GPa to 60 GPa, phonon bandwidth rises nearly 4-fold leading to the pressure-induced stiffening of Na. But the phonon bandwidth of Na in the fcc, cI16, or



FIG. 5. Phonon band structures, density of states (DOS), and the spectral function ( $\alpha^2 F$ ), for the four metallic phases. The phonon density of states is given in units of number of states/(cm<sup>-1</sup>/atom). Panel (a) plots the phonon band structure, DOS, and  $\alpha^2 F$  for the BCC phase at 0, 20, 40, and 60 GPa, (b) for the FCC phase at 100 GPa, (c) for the *cI*16 phase at 140 GPa, and (d) for the *tI*19 phase at 220 GPa.

tI19 structure does not change significantly with respect to pressure; in fact, it only increases from about 510 cm<sup>-1</sup> at 100 GPa in the fcc phase to 620 cm<sup>-1</sup> at 220 GPa in the tI19 phase.

In contrast to Li, the bcc-to-fcc phase transition in Na is not due to phonon softening but, rather, the Kohn anomalies in the phonon spectrum, which result in dynamic instability.<sup>6,42</sup> On the other hand, acoustic phonon softening along  $\Gamma K$ induces the fcc-to-cl16 transition in Na, which is similar to the fcc-to-cl16 transition in Li.<sup>40</sup> The cl16-Na and tl19-Na structures have 9 and 29 atoms in their primitive cells, respectively, therefore both of their phonon spectra are dominated by numerous optical phonon branches. The transition from cl16-Na to the open and incommensurate structure of tI 19-Na is explained by the Peierls distortions<sup>43</sup> and the localization of interstitial electrons,<sup>44</sup> whereas the strong s-p electron hybridization in Li leads to Fermi surface nesting and different phase transitions from the *cI*16 structure. Likewise, in the heavier alkali metals (K, Rb, and Cs), hybridization between the semi-core p states and valence d states contributes to the emergence of Fermi surface nesting as pressure increases.<sup>17,45</sup>

#### C. Superconductivity

As mentioned in Section I, we adopted Migdal-Eliashberg theory to compute the electron-phonon coupling constant,  $\lambda$ , by integrating the electron-phonon spectral function,  $\alpha^2 F(\omega)$ , according to Eq. (5). The spectral functions evaluated using Eq. (4) for the bcc, fcc, cI16, and tF19 phases are plotted in Fig. 5 in comparison with phonon DOS distribution,  $F(\omega)$ . In general,  $\alpha^2 F(\omega)$  and  $F(\omega)$  have very similar distributions except that the low-frequency peak positions in  $\alpha^2 F(\omega)$  vary with pressure in a slightly different way than those in  $F(\omega)$ because of the larger weights of the low-frequency terms in summation of Eq. (4).

The most important physical quantity entering the McMillan equation [Eq. (6)] is the electron-phonon coupling constant,  $\lambda$ , which is plotted in Fig. 6(b) as a function of pressure. A good superconductor normally has a  $\lambda \gtrsim 1$ ; however,  $\lambda$ peaks at only ~0.5 for P = 130 GPa in cI16-Na. Fig. 6(a) shows that the electronic DOS at the Fermi level tends to decrease as pressure increases due to the lack of *sp-d* hybridization under pressures up to 260 GPa, as previously discussed. Fig. 6(c) summarizes the calculated logarithmic averaged phonon frequency,  $\omega_{log}$ , whose trend can be understood by the relationship  $\langle \omega^2 \rangle \propto BV^{1/3}$ , where *B* and *V* are the bulk modulus and unit cell volume, respectively.

We plotted the critical temperature,  $T_c$ , of Na for pressures in the range of 0–260 GPa, as shown in Fig. 6(d). For the bcc and fcc structures, our results are in decent agreement with Christensen and Novikov,<sup>15</sup> while  $T_c$  of fcc-Na obtained by Shi *et al.* is about 1/2 to 1/3 of our value, as they used the RMTA to compute  $\lambda$  instead of evaluating the electron-phonon interactions directly.  $T_c$  of *cl*16-Na is slightly higher than that of fcc-Na near the transition pressure due to a slightly enhanced  $\lambda$ , while  $T_c$  of *tl*19-Na quickly approaches zero (0.053 K at 180 GPa) because of a significantly reduced  $\lambda$ .

Since current methods tend to overestimate superconductivity of alkali metals, especially for the peak values of  $T_c$ , our present investigation suggests that Na is unlikely to be a



FIG. 6. (a) Electron density of states at the Fermi level  $[N(\varepsilon_f)]$ , in units of number of states/(eV/bohr<sup>3</sup>), (b) electron-phonon coupling constant  $(\lambda)$ , (c) logarithmic averaged phonon frequency  $(\omega_{\log})$ , and the critical temperature  $(T_c)$  as functions of pressure for the four metallic phases. Circles and squares are computed data points, while the solid curves are the visual guides rather than true fits.

superconductor with a measurable critical temperature even under high pressure. This is at odds with other alkali metals including Li, K, Rb, and Cs. Among them Li has the highest  $T_c$  between 14 and 17 K in the cI16 phase,<sup>8–10</sup> which is mainly attributed to strong *s-p* hybridization.<sup>14,15,18–20</sup> In K, Rb, and Cs, the compression-induced *s-p* and *p-d* hybridizations contribute to superconductivity.<sup>15–18</sup> However, even at 260 GPa, the *p-d* hybridization in Na is nearly non-existent, as indicated by the spherical Fermi surfaces (Fig. 4). Although the *s-p* hybridization is enhanced by pressure, especially at the *cI*16 phase, the average phonon frequency of Na is much higher than that of Li<sup>17</sup> leading to a much smaller  $\lambda$  in *cI*16-Na than the  $\lambda$  of *cI*16-Li.

Furthermore, the lack of *d*-electron hybridization in Na leads to a decreasing  $N(\varepsilon_{\rm F})$  as pressure increases. According to the McMillan's theory,<sup>35,36</sup>

$$\lambda = \frac{N(\varepsilon_{\rm F})\langle I^2 \rangle}{M\langle \omega^2 \rangle},\tag{7}$$

where *M* is the atomic mass,  $\langle I^2 \rangle$  is the square of the electronion matrix element at the fermi level, and  $\langle \omega^2 \rangle$  is the averaged square of phonon frequency. Therefore, a reduction of  $N(\varepsilon_{\rm F})$ often lowers the value of  $\lambda$ .

Theoretical calculations place the metal-to-insulator transition at 260 GPa (~200 GPa in experiment) when the metallic tI19-Na becomes insulating hP4-Na. There is evidence of the  $p \rightarrow d$  electron transfer in the hP4 structure, but it also has a sizable band gap, larger than 1 eV.<sup>4,46</sup> A recent publication by Li *et al.*<sup>47</sup> reported the surprising re-entrance of Na into a metallic icosahedron phase (body-centered cubic cI24) at 15.5 TPa, and Na in this new metallic structure could become a superconductor. However, 15.5 TPa is beyond any current experimental feasibility, so we conclude that Na under high pressure (<15 TPa) is unlikely to be a measurable superconductor.

#### **IV. SUMMARY**

In light of the discovery of superconductivity in Cs and, especially, Li at high pressures, the alkali metals have received considerable attention from both a superconductivity stand point and from structural phase transition studies. Despite the fact that Na shares many similarities with the other alkali metals, such as crystal phases and electronic structures under ambient and low pressures, we show that Na exhibits weak superconductivity under pressures as high as 260 GPa, where the metal-to-insulator transition occurs. Theoretically, the peak critical temperature of Na is ~1 K in the *cI*16 phase, where as the maximum  $T_c$  K of other alkali metals under high pressure is  $T_c \gtrsim 6-20$  K.

This departure from the majority behavior of alkali metals is due to the fact that Na is the second lightest and simplest alkali metal next to Li. Under high pressure, enhanced *s-p* hybridization and the structural softening (lower average phonon frequency) in Li lead to its high  $T_c$ , but Na's bcc structure stiffens when pressure is applied. On the other hand, high pressure induces the *sp-d* hybridization for alkali metals heavier than Na, whereas there is almost no such hybridization in Na before the metal-to-insulator transition, as evident by the spherical Fermi surfaces in bcc, fcc, *cI*16, and *tI*19 phases and by the decreasing  $N(\varepsilon_F)$ .

Gatti *et al.*<sup>5</sup> argued that Na behaved counterintuitively under pressure because it favors less symmetric structures at ultrahigh pressures than other alkali metals due to the existence of *p*-states in the core, which are eventually forced out to hybridize with the *d*-orbitals leading to higher total energy changes and less symmetric structures than those of Li.<sup>2,6</sup> Thus only under extremely high pressure (>15 TPa),<sup>47</sup> after the insulator-to-metal transition, could the *p-d* hybridization lead to noticeable superconductivity in Na. We are currently investigating this possibility.

### ACKNOWLEDGMENTS

This work was supported by U.S. DOE Early Career Award (Grant No. DE-SC0006433) and the startup funding from Colorado School of Mines (CSM). Computations were carried out at the Golden Energy Computing Organization at CSM and the National Energy Research Scientific Computing Center (NERSC). The authors thank M. Lusk and D. Wood for their insight and discussion.

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