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Ab initio calculation of the lattice specific heat of lithium

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We have made a first-principles calculation of the lattice specific heat of lithium. We calculated the interionic potential using a first-principles pseudopotential which was constructed from the induced electron density around a lithium ion in an electron gas. This induced electron density was calculated fully self-consistently with the use of density-functional formalism. From the interionic potential we obtained the phonon dispersion curve using the harmonic and the self-consistent harmonic approximations. Then we obtained the phonon frequency distribution and the lattice specific heat. The results of the calculation are in good agreement with the experimental results.

I. INTRODUCTION

One of the main contributions to the specific heat of metals comes from the ion lattice. The first step in our calculation is to obtain the interionic potential. In previous work[1] we had performed a first-principles calculation of the interionic potential of lithium without using pseudopotentials, following a method based on the density-functional formalism[2,3] with no adjustable parameters. This had been applied previously with success to metallic hydrogen.[4,5] The phonons generated from that interionic potential were not completely satisfactory[1] and were not used to calculate the lattice specific heat or any other property of lithium.

For simple metals the interionic potential can be constructed from first principles using pseudopotential theory.[6,7] We construct a first-principles local pseudopotential following the method proposed by Manninen *et al.*,[7] who followed the work of Rasolt and Taylor,[6] with some differences.

In the approach of Rasolt and Taylor,[6] the displaced electronic density around an ion in an electron gas is calculated with the use of nonlinear screening theory and the full electron-ion potential. Then a nonlocal pseudopotential is selected in order to reproduce, as closely as possible, the nonlinear displaced electronic density by linear-response theory, except in the vicinity of the ion. In this way the nonlinear effects are partly included in the pseudopotential. The interionic potentials calculated using these pseudopotentials have been used with success to calculate phonon dispersion curves in simple metals.[8,9]

In the method of Manninen *et al.*,[7] a Fourier transform of the displaced electronic density around an impurity in an electron gas is taken. Then a local pseudopotential is defined in such a way that it reproduces exactly, in linear-response theory, this displaced electronic density. They considered the screening of the ion as calculated for two models: one where the ion is embedded in a homogeneous electron gas and one where the ion is embedded in a jellium vacancy. They found this second model to describe much better the cohesion in the metal. From the calculated pseudopotentials they obtained the interionic potential. Then, they calculated the total energy of the metal, the equilibrium lattice constant, the bulk modulus, the vacancy-formation energy, and the electrical resistivity of the liquid phase. The metal they considered was aluminum. In a more recent work, Jena, Sterling, and Manninen[10] made a calculation of the phonon dispersion curve of aluminum using the interionic potential for this material reported by Manninen *et al.*[7] for the model of the nucleus embedded in a jellium vacancy. They did not calculate the phonon spectrum nor the specific heat.

In this work we applied the method of Manninen *et al.*[7] to lithium in order to obtain a first-principles local pseudopotential. From the pseudopotential we calculated the interionic potential. Then, using the harmonic and the self-consistent harmonic approximations[11-13] we obtained the phonon dispersion curve and the phonon spectrum for lithium and from this, the specific heat.

In Sec. II we present the equations of the density-functional formalism we solved for the two models of the impurities in the electron gas: the nucleus embedded in a homogeneous electron gas and the nucleus embedded in a jellium vacancy.[7,14,15]

In Sec. III we outline the method of Manninen *et al.*[7] for smoothing the displaced electron densities to construct the pseudopotential and give the dielectric function we use. Section IV is used to present the set of equations to be solved in the self-consistent harmonic approximation[11-13] in order to obtain the phonon dispersion curve. In this section we also outline the method of constructing the phonon spectrum to obtain the specific heat. Results and discussion are given in Sec. V.

II. DISPLACED ELECTRON DENSITIES

To calculate the displaced electron densities we use the formalism of Hohenberg, Kohn, and Sham.[2,3] The central result of this formalism states that there exists a one-body local potential $V_{\text{eff}}(\mathbf{r})$, which through a one-body Schrödinger equation

$$[-\tfrac{1}{2}\nabla^2+V_{\text{eff}}(\mathbf{r})]\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r}) , \tag{1}$$

generates the set of wave functions $\psi_i(\mathbf{r})$ and the exact ground-state density of the system.

The effective potential is

$$V_{\text{eff}}(\mathbf{r})=-\Phi(\mathbf{r})+\frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})} , \tag{2}$$

where $\Phi(\mathbf{r})$ is the total electrostatic potential and $E_{\text{xc}}[n(\mathbf{r})]$ is the exchange-correlation energy of the system.

For the exchange-correlation contribution to the effective potential Eq. (2), we use the expression given by Gunnarson and Lundquist[16] in atomic units (two rydbergs):

$$\begin{aligned}V_{\text{xc}}(\mathbf{r})&\equiv\frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}\\&=-0.6109\left[\frac{1}{r_s}+0.0545\ln\left[1+\frac{11.4}{r_s}\right]\right] ,\end{aligned} \tag{3}$$

where $\frac{4}{3}\pi r_s^3=1/n$.

In order to have $V_{\text{eff}}(\mathbf{r})$ vanish at large r, the exchange-correlation part is rescaled to

$$V_{\text{xc}}(\mathbf{r})\rightarrow V_{\text{xc}}[n(\mathbf{r})]-V_{\text{xc}}[n_0] . \tag{4}$$

The electrostatic potential obeys Poisson's equation

$$\nabla^2\Phi=-4\pi D(\mathbf{r}) , \tag{5}$$

where $D(\mathbf{r})$ is the total charge density.

If we consider that the nucleus is embedded in a homogeneous electron gas

$$D(\mathbf{r})=Z\delta(\mathbf{r})+n_0-n(\mathbf{r})=Z\delta(\mathbf{r})=\Delta n(\mathbf{r}) , \tag{6}$$

where $\delta(\mathbf{r})$ is the Dirac δ function. If the nucleus is located at the center of a vacancy in jellium

$$D(\mathbf{r})=Z\delta(\mathbf{r})+n_0\Theta(r-R_{\text{WS}})-n(\mathbf{r}) , \tag{7}$$

where $\Theta(x)$ is the step function, and R_{WS} is the Wigner-Seitz radius.

III. THE PSEUDOPOTENTIAL

The unscreened pseudopotential form factor $v(q)$ is related to the Fourier transform of the induced charge pseudodensity $n(q)$ by

$$v(q)=\frac{4\pi\delta n(q)\epsilon(q)}{q^2[1-\epsilon(q)]} , \tag{8}$$

where $\epsilon(q)$ is the dielectric response function.

We calculate $\delta n(q)$ using the induced density $\delta n(\bar{r})$ computed by the density-functional formalism,[2,3] with smoothing in a region near the origin.[7] Then, Eq. (8) is used to obtain an effective local pseudopotential, which in linear-response theory will give the exact induced density outside the region of smoothing. In this way some of the nonlinear screening effects are included into the pair potential calculated from the pseudopotential.[6,7] It should be remarked that in the pseudopotential formulation, the pseudodensity must not have core orbitals. In this way the pseudodensity must not contain wiggles near the ion. The wiggles near the ion would appear because of the orthogonalization of conduction states to core orbitals.

For a given unscreened pseudopotential form factor $v(q)$, which is assumed to be weak, the interionic potential, in second-order perturbation theory and linear-response theory is[17]

$$\Phi(r)=\frac{Z^2}{r}\left[1+\frac{2}{\pi Z^2}\int_0^\infty\frac{dq\,\sin(qr)\epsilon(q)[\delta n(q)]^2}{q[1-\epsilon(q)]}\right] , \tag{9}$$

where r is the separation between the two ions and Z is the charge of the metal ion.

The induced density around an ion, when we consider the nucleus embedded in a homogeneous electron gas, is defined as

$$\delta n(\mathbf{r})=n(\mathbf{r})-2\sum_b|\psi_b(\mathbf{r})|^2-n_0 , \tag{10}$$

where $n(\mathbf{r})$ is the total electron density calculated with the total charge density given by Eq. (6) and $\psi_b(\mathbf{r})$ refers to the bound electron wave function.

For the case of the nucleus embedded in a jellium vacancy, the induced density is calculated by taking the difference[7]

$$\delta n(\mathbf{r})=n(\mathbf{r})-n_v(\mathbf{r})-2\sum_b|\psi_b(\mathbf{r})|^2 , \tag{11}$$

where $n(\mathbf{r})$ is calculated with the total charge density given by Eq. (7) and $n_v(\mathbf{r})$ is the electron density around a jellium vacancy and corresponds to an external positive background charge density

$$D^+(\mathbf{r})=n_0\Theta(r-R_{\text{WS}}) .$$

For both expressions for the induced electron density, charge neutrality requires that

$$\int\delta n(\mathbf{r})dv=Z ,$$

where Z is the valence of the ion in the metal.

The induced density calculated from the density-functional formalism contains wiggles at small $\mathbf{r}$ as a result of the orthogonalization of conduction states to core orbitals. We have smoothed our calculated induced density, following the method of Manninen *et al.*,[7] without introducing any adjustable parameter in the smoothing procedure. This is achieved by using a second-order polynomial given by

$$\delta n(\mathbf{r})=A-Br^2,\quad r\leq R_0 \tag{12}$$

for small values of r. The constants A, B, and R_0 are calculated with the conditions that $\delta n(\mathbf{r})$ and $(\partial/\partial r)[\delta n(\mathbf{r})]$ are continuous at $r=R_0$ and that the electronic charge is conserved. The smoothed density is the one we used as the pseudodensity in Eq. (9) to calculate the interionic potential.

The dielectric function we used satisfies, by construction, the compressibility theorem which is important in connection with the interionic potential.[7,18] The dielectric function is given by

$$\epsilon(q)=1+\left[\frac{4\pi}{q^2}\right]G(q)\ , \tag{13}$$

where

$$G(q)=\frac{G_0(q)}{1-(4\pi/K_{\mathrm{TF}}^2)G_0(q)(1-L)}\ ,$$

where $G_0(q)$ is the usual Lindhard polarizability, K_{TF} is the Thomas-Fermi screening constant, and

$$L=\left[\frac{\partial\mu}{\partial r_s}\right]\Big/\left[\frac{\partial\epsilon_F}{\partial r_s}\right]\ . \tag{14}$$

In Eq. (14) μ is the chemical potential, ϵ_F is the Fermi energy, and

$$\mu(r_s)=\epsilon_F(r_s)+\mu_{\mathrm{xc}}(r_s)\ ,$$

where $\mu_{\mathrm{xc}}(r_s)$ is the exchange-correlation contribution to the chemical potential.

Using the expression of Gunnarson and Lundquist[16] for exchange correlation (which we used in the calculation of the induced density), the corresponding value of L is

$$L=1-\left[\frac{1}{9\pi^4}\right]^{1/3}r_s\left[1+\frac{0.6213r_s}{r_s+11.4}\right]\ . \tag{15}$$

IV. PHONONS AND SPECIFIC HEAT

Having the induced pseudodensity and the dielectric function, we can use Eq. (9) to calculate the interionic potential.

From the interionic potential we calculate the phonon dispersion curves from the self-consistent harmonic approximation.[11–13] In this approximation, in contrast with that of Born and Von Kárman,[19,20] there is not an initial hypothesis of smallness for the amplitude of atomic vibrations and hence no truncated Taylor-series expansion of the interatomic potential energy.

The resulting set of self-consistent equations to solve in order to obtain the phonon dispersion curve is the following:

$$\omega_\lambda^2(\mathbf{k})\epsilon_\lambda^\alpha(\mathbf{k})=\sum_\beta D_{\alpha\beta}(\mathbf{k})\epsilon_\lambda^\beta(\mathbf{k})\ , \tag{16}$$

where $\epsilon_\lambda^\alpha(\mathbf{k})$ is the component of the polarization vector $\epsilon_\lambda(\mathbf{k})$ and the dynamical matrix is

$$D_{\alpha\beta}(\mathbf{k})=\frac{1}{M}\sum_l[1-\cos(\mathbf{k}\cdot\mathbf{R}_l)]\langle\Phi_{\alpha\beta}(\mathbf{R}_l)\rangle\ , \tag{17}$$

with

$$\langle\Phi_{\alpha\beta}(\mathbf{R}_l)\rangle=\frac{1}{(8\pi^3\det\lambda_l)^{1/2}}\times\int d^3\mu\,\exp\left[-\tfrac{1}{2}\sum_{\gamma,\delta}\mu_\gamma(\lambda_l^{-1})_{\gamma\delta}\mu_\delta\right]\times\Phi_{\alpha\beta}(\mathbf{R}_l+\boldsymbol{\mu}_l)\ , \tag{18}$$

where M is the ion mass, $\boldsymbol{\mu}_l$ is the vector describing the displacement of atom l from its equilibrium position $\mathbf{R}_l$, and $\Phi_{\alpha\beta}(\mathbf{R}_l+\boldsymbol{\mu}_l)$ is the tensor derivative of the interatomic potential evaluated at $\mathbf{R}_l+\boldsymbol{\mu}_l$. Finally

$$(\lambda_l)_{\alpha\beta}=\frac{1}{MN}\sum_{\mathbf{k},\lambda}[1-\cos(\mathbf{k}\cdot\mathbf{R}_l)]\epsilon_\lambda^{*\alpha}(\mathbf{k})\epsilon_\lambda^\beta(\mathbf{k})\times\coth[\tfrac{1}{2}\beta\hbar\omega_\lambda(\mathbf{k})]/\omega_\lambda(\mathbf{k})\ , \tag{19}$$

where N is the number of ions. The sum is over the first Brillouin zone, β is $1/k_BT$, k_B being Boltzmann's constant.

TABLE I. Phase shifts η_l, Friedel sum (FS), and binding energy (BE) for lithium $r_s=3.236a_0$ with $a_0=0.529$ Å. We have three cases: nucleus in a homogeneous electron gas (NHG); nucleus embedded in a jellium vacancy (NJV); vacancy in jellium (VJ).

	NHG	NJV	VJ
η_0	3.2171	2.8472	−0.6726
η_1	0.4877	0.1391	−0.2226
η_2	0.0112	−0.0162	−0.0417
η_3	−0.0008	−0.0045	−0.0036
η_4	0.0007	0.0001	0.0000
FS	3.0131	2.0074	−1.0022
BE (Ry)	−3.1582	−3.0474	

To solve the set of self-consistent equations (16)–(19) we start with the frequencies generated by the harmonic approximation as the first trial. Then the convergence procedure is followed.

To calculate the phonon frequency distribution $F(\nu)$, from the force constants obtained in the phonon dispersion curve we followed the method of Gilat and Raubenheimer.[21] This method consists of solving the secular equation associated with the dynamical matrix only at a relatively small number of points in the irreducible part of the first Brillouin zone. Then, by means of linear extrapolation the other phonon eigenfrequencies are extracted from within small cubes, each centered at one point. These cubes are arranged to fill the entire irreducible part of the first Brillouin zone and thus yield the complete frequency distribution of the crystal.

Having the phonon spectrum $F(\nu)$, the specific heat at constant volume is calculated by the integral (numerically solved)

$$C_v=\frac{\partial\langle E\rangle}{\partial T}=k_B\int_0^{\nu_m}d\nu\left[\frac{\beta h\nu}{2}\right]^2\frac{F(\nu)}{\sinh(\beta h\nu/2)}\ , \tag{20}$$

where $\langle E\rangle$ is the average of the internal energy, T is the temperature, and ν_m is the maximum phonon frequency.

V. RESULTS AND DISCUSSION

The first step was to calculate the induced electron density for lithium. We did this using two models: a nucleus in a homogeneous electron gas and a nucleus in a jellium vacancy. Notice that in order to obtain $\delta n(\mathbf{r})$ from Eq. (11) we need to calculate the electron density around a jellium vacancy and around a nucleus in a jellium vacancy. We calculated the electron densities fully self-consistently. The Schrödinger equation was solved in steps of $0.01a_0$, where a_0 is the Bohr radius ($a_0=0.529$ Å), up to $R_{\max}=15.04a_0$, where the phase shifts were evaluated. Table I shows the values for the phase shifts η_l and the Friedel sum rule (FSR) for the calculation of the electron density for the three cases we have considered. We can see that the $1S^2$ bound state has an energy closer to zero for the case of a nucleus in a jellium vacancy because of the repulsive potential introduced by the vacancy.

The following step was to evaluate the Fourier transform of the smoothed densities. Since this implies knowing $\delta n(r)$ up to infinity, we used the asymptotic form for $\delta n(r)$ beyond $R_{\max}=15.04a_0$, given by

$$\delta n(r)=A\cos(2k_F r+\phi)/r^3 ,$$

where the constants A and ϕ were obtained using the last points in our calculation of $\delta n(r)$. In order to test the accuracy of our Fourier transform we obtained $\delta n(r)$ by taking the inverse Fourier transform of $\delta n(q)$ and the difference with respect to the original values of $n(r)$ was less than 0.08%.

With $\delta n(q)$ and the dielectric function corresponding to the expression for exchange correlation energy given by Gunnarson and Lundquist,[16] we can obtain the interionic potential using Eq. (9). Figure 1 shows the resulting interionic potentials from the two models. We can notice from this figure that the potential resulting from the model of the nucleus embedded in a jellium vacancy has a minimum which is less deep than the corresponding to the other model and has oscillations of smaller amplitude.

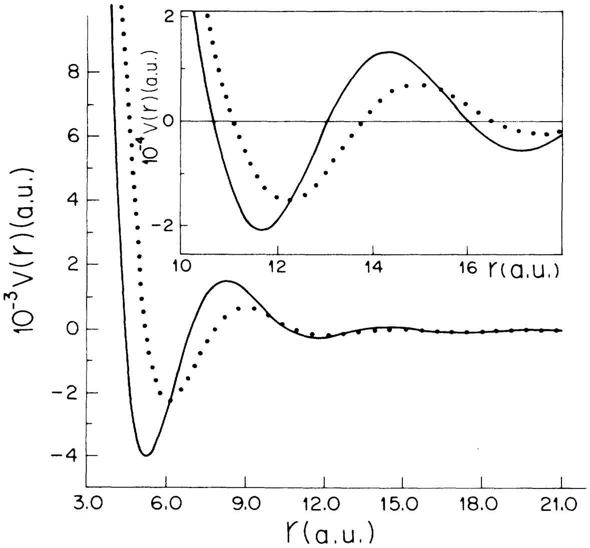

FIG. 1. Calculated interionic potential for lithium. Model of a nucleus embedded in a homogeneous electron gas, ——; model of a nucleus embedded in a jellium vacancy, · · ·.

From the interionic potentials we calculated the phonon dispersion curves using the self-consistent harmonic approximation.[11–13] Figure 2 shows the phonon dispersion curve obtained from the interionic potential calculated for the model of the nucleus embedded in a homogeneous electron gas. Figure 2 also shows a comparison with experiment.[22] The theoretical predictions using this model are not good. The overall shape is not satisfactory and the magnitude of the maximum frequencies for the $[qqq]$ and $[qq0]$ branches are not satisfactory either.

The phonon dispersion curve obtained from the interionic potential resulting from the model of the nucleus embedded in a jellium vacancy is in good agreement with experimental results[22] as it is shown in Fig. 3. The curves have the same overall shape as the corresponding experimental results and the values of the maximum frequencies are satisfactory, and the differences between the frequencies generated using the harmonic approximation and those generated using the self-consistent harmonic approximation are very small (about 1%). The force constants obtained for this case were used to calculate the phonon spectrum $F(\nu)$.

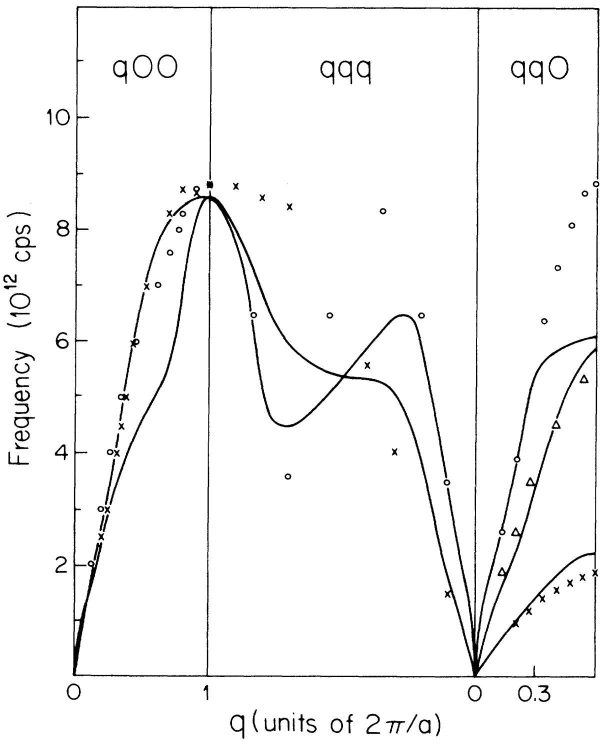

FIG. 2. Phonon dispersion curve for the interionic potential calculated with the model of the nucleus embedded in a homogeneous electron gas, ——; experimental results (Ref. 22) X, 0, $\triangle$.

TABLE II. Result of the calculation of the specific heat of lithium in units of cal/K mol in the third column. Experimental results (Ref. 24) after the correction of the electronic contribution (Ref. 25) are given in the second column. The temperature is in the first column.

T (K)	C_v(expt)	C_v(calc)	C_v(calc)/C_v(expt)
90	2.70	2.47	0.915
95	2.88	2.64	0.917
100	3.04	2.81	0.924
120	3.62	3.39	0.936
140	4.08	3.86	0.946
160	4.40	4.23	0.961
180	4.73	4.51	0.953
200	4.96	4.74	0.956
220	5.13	4.92	0.959
240	5.28	5.07	0.960
260	5.40	5.18	0.959
280	5.52	5.28	0.956
300	5.62	5.36	0.954

The specific heat obtained from the phonons calculated using the harmonic approximation and the one obtained from the phonons generated using the self-consistent harmonic approximation are practically identical and in good agreement with experiment.

There is a more precise way of calculating phonon dispersion curves for lithium[23] which consists in adding a cubic anharmonic term as a perturbation to the self-consistent harmonic approximation but the large amount of computation required makes a specific heat calculation very expensive. On the other hand, the fact that the difference between the frequencies generated using these two approaches is very small indicates that the difference between our results and experiment is not due to anharmonic contributions. We should also mention that our main purpose in this work is not to study the anharmonic effects but to assess the applicability of our pseudopotential.

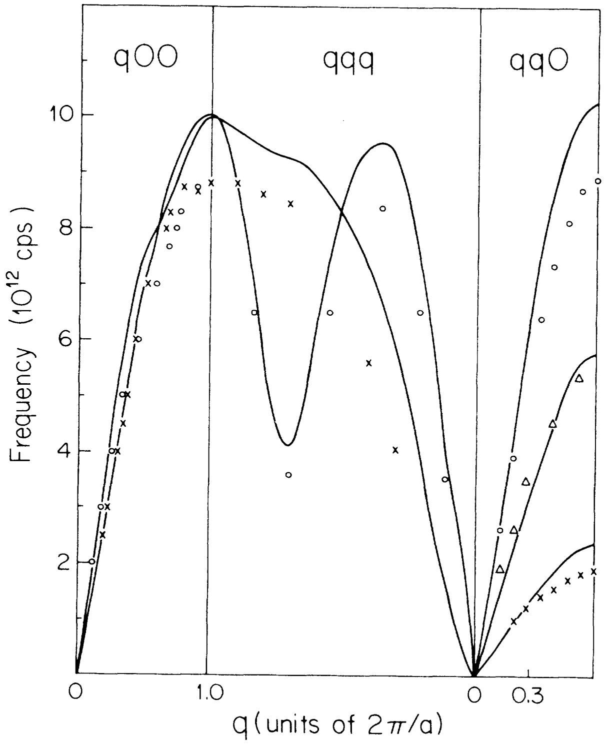

FIG. 3. Phonon dispersion curve for the interionic potential calculated with the model of the nucleus embedded in a jellium vacancy, ——; experimental results (Ref. 22) X, 0, $\triangle$.

Lithium retains its normal bcc structure for temperatures above about 80 K.[24] For temperatures below this a partial transformation of the martensitic type to a hcp structure with stacking faults, takes place.[24] Table II shows the result of our calculation of the lattice specific heat of lithium for temperatures of 90 K and above. The experimental results were taken from Ref. 24 with corrections for the electronic contribution taken from Ref. 25. We can see that the calculated values of the specific heat are in good agreement with the experimental results.

As final comment, we could not find any other first-principles calculation of the specific heat of lithium. However, in Ref. 26 there is a calculation of this property of lithium using a phenomenological local pseudopotential. The difference between the calculated values and experiment is about the same ($\sim 8\%$) we obtained in this work.

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