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Volume dependence of the superconducting transition temperature of aluminum calculated from a first-principles potential

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Using a first-principles, local, volume-dependent pseudopotential which has been used successfully to calculate several properties of aluminum, we have calculated the electron-phonon interaction for this material. From this information we have calculated the volume dependence of the superconducting transition temperature. The pseudopotential is constructed from the nonlinear induced density around an aluminum ion in an electron gas. The volume dependence is introduced by the electron-gas density parameter r_s.

I. INTRODUCTION

To have a reliable, first-principles, pressure-dependent interionic potential is very important to make predictions of the behavior of materials under pressure. With this in mind we had performed, in previous work,[1,2] first-principles calculations of the interionic potentials of lithium and aluminum, using a method which had been applied with success to metallic hydrogen.[3,4] However, the phonon frequencies calculated using those interionic potentials were not satisfactory and could not be used to calculate any property of aluminum or lithium.

In more recent work we have calculated the interionic potentials for aluminum and lithium using first-principles pseudopotentials. These potentials were used to calculate the specific heat of lithium and the pressure dependence of the specific heat of aluminum successfully.[5,6] The pseudopotentials were calculated from first principles following a method proposed by Manninen *et al.*[7] who followed some basic ideas from the work of Rasolt *et al.*[8]

In this work we follow the same method of Manninen *et al.*[7] to obtain a local, first-principles, pressure-dependent pseudopotential to construct the interionic potential. Then, we calculate the force constants associated with this interionic potential using the self-consistent harmonic approximation[9,10] (SCHA). These force constants and the pseudopotential are used to calculate the effective phonon distribution function $\alpha^2F(\omega)$. From this function we calculate the superconducting transition temperature, T_c, using the formula proposed by McMillan[11] and the method proposed by Leavens.[12] The whole procedure, i.e., the calculation of the first-principles pseudopotential, then the interionic potential, the force constants and T_c, is done for five different values of the electron density parameter r_s: the value at atmospheric pressure, and then for values which are 1%, 2%, 3%, 4%, and 5% smaller.

In Sec. II we make a brief description of the method we have followed to construct the pseudopotential. Section III is used to briefly describe the phonons in the SCHA, the effective phonon distribution function $\alpha^2F(\omega)$, and the formulas to calculate T_c. Section IV is used for results and conclusions.

II. THE PSEUDOPOTENTIAL

Here we will give a brief description of the method used to construct the pseudopotential. For further details the reader may see Refs. 6 and 7.

In this method 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, except for a small region very close to the ion, the displaced electronic density. In this way some of the nonlinear screening effects are included into the interionic potential calculated from the pseudopotential.[7]

The relationship between the Fourier transform of the induced charge pseudodensity and the unscreened pseudopotential form factor $v(q)$ is

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

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

From pseudopotential theory and linear-response theory,[13] the interionic potential $\Phi(\mathbf{r})$ is given by

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

where Z is the charge of the metal ion and $\mathbf{r}$ is the separation between ions.

In order to obtain $\delta n(q)$ we have considered the model of a nucleus embedded in a jellium vacancy[7,14,15] (this model describes the phonons and the cohesion in the metal much better than the model of the nucleus embedded in a homogeneous electron gas[6,7]). We first calculated the electron density $n(\mathbf{r})$ in an electron gas perturbed by an aluminum nucleus located at the center of a spherical vacancy made in the positive background and we also calculated the electron density, $n_v(\mathbf{r})$, around a pure jellium vacancy. Then, we calculated the difference

$$\Delta n(\mathbf{r}) = n(\mathbf{r}) - n_v(\mathbf{r}) - 2\sum_b |\psi_b(\mathbf{r})|^2 , \tag{3}$$

where $\psi_b(\mathbf{r})$ refers to the bound-electron wave functions. The calculation of the electron densities was performed using the density-functional formalism.[16,17] The induced density $\Delta n(\mathbf{r})$ has wiggles for small values of r due to the orthogonalization of conduction states to core orbitals. However, in the pseudopotential formulation the pseudodensity must not have core orbitals, thus we smoothed $\Delta n(r)$ in order to remove the wiggles near the ion following the method of Manninen *et al.*,[7] using a second-order polynomial, $\delta n(r) = A - Br^2$, $r \le R_0$, for small values of r. The constants A, B, and R_0 are determined under the conditions that $\delta n(r)$ and $\partial[\delta n(r)]/\partial r$ are continuous at R_0 and that the electronic charge is conserved. This smoothed density is the pseudodensity we used in Eqs. (1) and (2) to calculate the pseudopotential and the interionic potential, respectively.

The dielectric function we used satisfies the compressibility theorem, which is important in connection with the interionic potential,[7,18] and involves the expression given by Gunnarsson and Lundqvist for the exchange correlation energy[19] (which is the same we have used in the calculation of the induced nonlinear densities). The dielectric function is given by

$$\epsilon(q) = 1 + (4\pi/q^2)G(q) ,$$

where

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

and $G_0(q)$ is the usual Lindhard polarizability and k_{TF} is the Thomas-Fermi screening constant. The expression for L is

$$L = \frac{\partial\mu/\partial r_s}{\partial E_F/\partial r_s} ,$$

where μ is the chemical potential, E_F is the Fermi energy, and

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

where $\mu_{\mathrm{xc}}(r_s)$ is the exchange-correlation contribution to the chemical potential. Using the expression of Gunnarsson and Lundqvist for exchange-correlation, the value of L is given by

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

III. ELECTRON-PHONON INTERACTION AND T_c

From the interionic potential we calculated the corresponding force constants using the SCHA.[9,10] The resulting set of equations to be solved in the SCHA is the following:

$$\omega_\lambda^2(\mathbf{k})\epsilon_\lambda^\alpha(\mathbf{k}) = \sum_\eta D_{\alpha\eta}(\mathbf{k})\epsilon_\lambda^\eta(\mathbf{k}) , \tag{4}$$

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

$$D_\alpha(\mathbf{k}) = \frac{1}{M}\sum_l [1 - \cos(\mathbf{k}\cdot\mathbf{R}_l)]\langle\Phi_\alpha(\mathbf{R}_l)\rangle , \tag{5}$$

with

$$\langle\Phi_{\alpha\eta}(\mathbf{R}_l)\rangle = \frac{1}{(8\pi^3 \det\lambda_l)^{1/2}} \int d^3\mu \exp\left[-\tfrac{1}{2}\sum_{\gamma,\delta}\mu_\gamma(\lambda_l^{-1})_{\gamma\delta}\mu_\delta\right]\Phi_{\alpha\eta}(\mathbf{R}_l + \boldsymbol{\mu}_l) , \tag{6}$$

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,

$$(\lambda_l)_{\alpha\eta} = \frac{1}{MN}\sum_{\mathbf{k},\lambda} [1 - \cos(\mathbf{k}\cdot\mathbf{R}_l)]\epsilon_\lambda^{*\alpha}(\mathbf{k})\epsilon_\lambda^\eta(\mathbf{k})\coth[\tfrac{1}{2}\beta h\omega_\lambda(\mathbf{k})]/\omega_\lambda(\mathbf{k}) , \tag{7}$$

where N is the number of ions. The sum is over the first Brillouin zone and β is $1/(k_B T)$, k_B being the Boltzmann constant.

To solve the set of self-consistent equations (4)–(7) we start with the frequencies generated by the harmonic approximation as the first trial. Then the convergence procedure is followed. From the solution to these equations we obtain the force constants to be used in our calculation of the effective phonon distribution function $\alpha^2F(\omega)$ which is useful to calculate T_c.

The function $\alpha^2F(\omega)$ can be expressed as[20]

$$\alpha^2F(\omega) = N(O)\int \frac{d\Omega_k}{4\pi}\frac{d\Omega_{k'}}{4\pi} \times \sum_\lambda |g_{\mathbf{kk}',\lambda}|^2 \delta(\omega - \omega_\lambda(\mathbf{k}-\mathbf{k}')) , \tag{8}$$

where $N(O)$ is the electron density of states at the Fermi level, $d\Omega_k$ and $d\Omega_{k'}$ are solid-angle elements on the Fermi surface at $\mathbf{k}$ and $\mathbf{k}'$, $\omega_\lambda(\mathbf{k}-\mathbf{k}')$ are the photon frequencies, and $g_{\mathbf{kk}',\lambda}$ is the electron-phonon coupling constant which, for the one-plane-wave theory, is given by

$$g_{\mathbf{kk}',\lambda} = -\frac{i\mathbf{q}\cdot\epsilon_\lambda(q)W_{kf}(q)}{[2MN\omega_\lambda(q)]^{1/2}} , \tag{9}$$

where $q = \mathbf{k} - \mathbf{k}'$, and $W_{kF}(q)$ is the form factor for scattering on the Fermi surface.

To calculate T_c we have used the formulas given by McMillan[11] and Leavens.[12] The equation for T_c given by McMillan is

$$k_B T_c = \frac{\langle \omega \rangle}{1.20} \exp\left[-\frac{1.04(1+\lambda)}{(\lambda - \mu^*)(1+0.62\lambda)} \right] , \tag{10}$$

where

$$\langle \omega \rangle = \frac{2}{\lambda} \int_0^\infty \alpha^2 F(\omega) d\omega , \tag{11}$$

and μ^* is the Coulomb pseudopotential parameter. The expression for λ is also given in terms of $\alpha^2 F(\omega)$:

$$\lambda = 2 \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega \tag{12}$$

and it is the electron-phonon mass-enhancement factor.

The expression for T_c given by Leavens[12] corresponds to a coupled pair of equations:

$$k_B T_c = 1.134 \omega_0 \exp\left[-\frac{1+\lambda+\bar{\lambda}(T_c)}{\lambda - \mu^*} \right] , \tag{13}$$

and

$$\bar{\lambda}(T_c) = 2 \int_0^{\omega_0} \frac{\alpha^2 F(\omega) d\omega}{\omega} \ln\left[\frac{\omega + \omega_0}{\omega + k_B T_c / 1.134} \right] , \tag{14}$$

where ω_0 is the maximum phonon frequency.

IV. RESULTS AND CONCLUSIONS

The whole procedure is started with the calculation of the displaced electronic density. This is done by first calculating the electron density $n(\mathbf{r})$ in an electron gas perturbed by an aluminum nucleus embedded in a spherical vacancy made in the positive background. Then, we calculated the electron density $n_v(\mathbf{r})$ around a jellium vacancy. The densities were obtained using the density-functional formalism.[16,17] The displaced electron density is obtained by Eq. (3). This displaced electron density is then smoothed in a region close to the ion following the procedure mentioned in Sec. II. This smoothed density is used as the pseudodensity. To obtain the Fourier transform of this pseudodensity we had to use the asymptotic form given by

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

where the constants A and ϕ were obtained using the last points of our numerical calculation of $\delta n(\mathbf{r})$. This numerical calculation of the density was up to $R_{\max} = 15.04 a_0$, where $a_0 = 0.529$ Å is the Bohr radius. To test the accuracy of the Fourier transform we obtained $\delta n(\mathbf{r})$ by taking the inverse Fourier transform of $\delta n(q)$ and the difference with respect to the original values of $\delta n(\mathbf{r})$ was less than 0.08%.

The pseudopotential, for each value of r_s, is obtained using $\delta n(q)$ and the dielectric function corresponding to the expression of exchange correlation energy given by Gunnarsson and Lundqvist,[19] in Eq. (1). The interionic potential is obtained using Eq. (2). In Fig. 1 we show the resulting interionic potential for three different values of r_s. The first is for atmospheric pressure, the second is for a value which is 2% smaller than the corresponding value at atmospheric pressure and the third is 4% smaller than the first value.

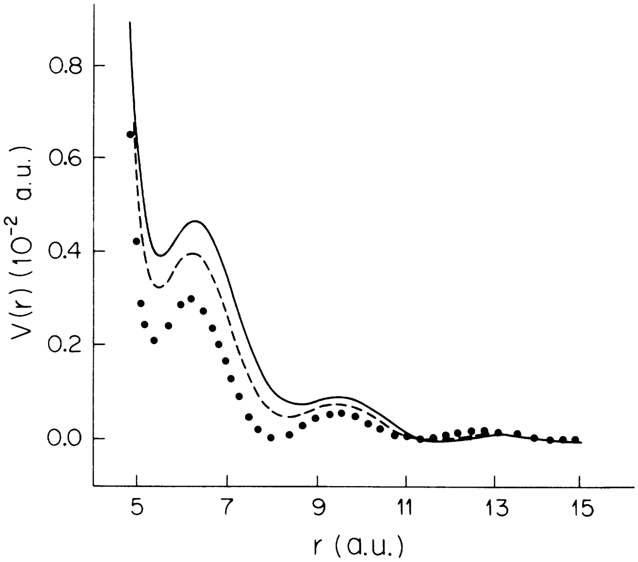

FIG. 1. Resulting interionic potential for aluminum as a function of pressure. For a value of r_s which corresponds to atmospheric pressure, ——; for a value of r_s which is 2% smaller, — — —; for a value of r_s which is 4% smaller, · · · .

From the interionic potential we calculated the corresponding force constants using the self-consistent harmonic approximation. We should mention that the phonons generated using this approximation are in good agreement with experimental results.[5]

The force constants are used to calculate the function $\alpha^2 F(\omega)$ by Eqs. (8) and (9). This is achieved following the method of Gilat and Raubenheimer[21] with some straightforward modifications. The method of Gilat and Raubenheimer[21] consists of solving the secular equation associated with the dynamical matrix only at a relatively small number of points of the irreducible part of the first Brillouin zone. Then, by using a 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.

With the function $\alpha^2 F(\omega)$ we calculate λ and $\bar{\lambda}(T_c)$ which are required to calculate T_c with the formulas of McMillan and Leavens [Eqs. (10)–(14)]. Figure 2 shows the function $\alpha^2 F(\omega)$. The corresponding value of λ at atmospheric pressure is 0.245 which is smaller than the values previously reported for λ $(0.364 \leq \lambda \leq 0.51)$, see Refs. 22–25.

The density dependence of the Coulomb pseudopotential parameter μ^* is not known, but it is believed to be small. We have considered a rescaling of the zero pressure value at each volume according to the simple expression obtained in Thomas-Fermi screening. This resulted in a small increase in μ^*. For for the zero-pressure value we considered five possibilities. The first one was taking the expression given in Refs. 26 and 27 which was 0.126 using Thomas-Fermi screening. The second value we

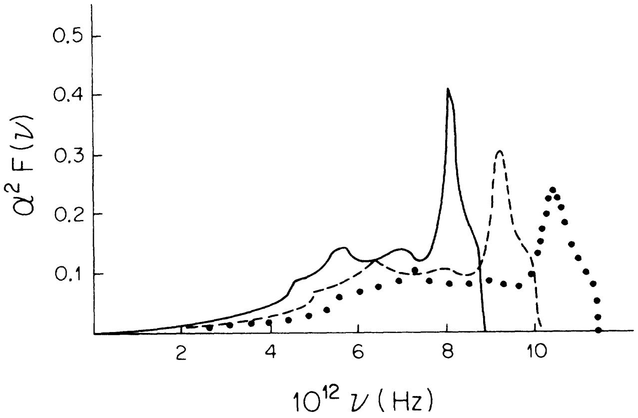

FIG. 2. The function $\alpha^2F(\omega)$ for electron-phonon interaction. For a value of r_s at atmospheric pressure, ——; for a value of r_s which is 2% smaller, — — —; for a value of r_s which is 4% smaller, · · · .

took for the zero-pressure value of μ^* was 0.10 and then 0.07, 0.05, and 0.001, respectively. In Fig. 3 we show the variation of $T_c/T_c(0)$ with volume change. We used the formula by McMillan [Eqs. (10)–(12)] and the formula by Leavens [Eqs. (12)–(14)]. The results, using one formula or the other, are very similar. The difference between the results from these formulas increases slightly as μ^* decreases. Figure 3 shows the results obtained using the formula by Leavens and, for the smallest value of μ^*, the result obtained using the formula of McMillan is also shown.

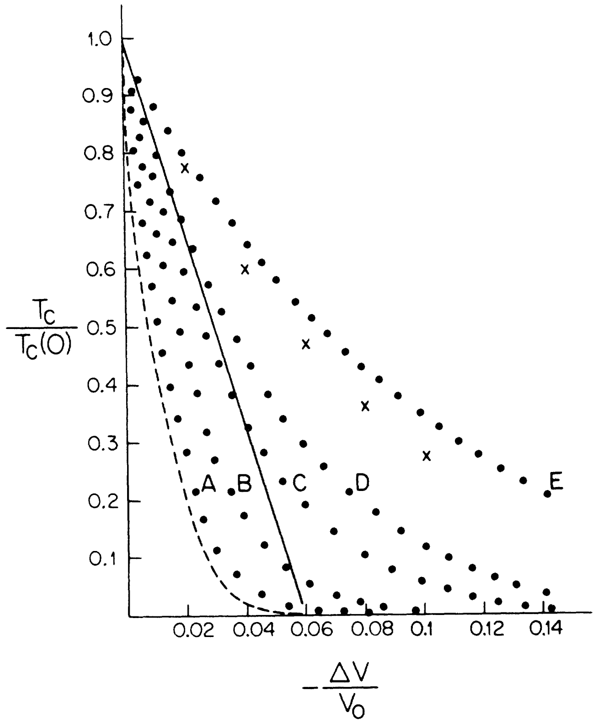

FIG. 3. Variation of the transition temperature with volume change. The solid line corresponds to experimental results from Ref. 28. Curve E corresponds to the prediction made in this work using the formula by Leavens. Curves A, B, C, and D are for different values of $\mu^*(0)=0.126$, 0.10, 0.02, and 0.05, respectively. For curve E, $\mu^*(0)=0.001$. The discontinuous curve corresponds to case A, using McMillan's formula. The crosses correspond to result of Ref. 29.

It is clear from Fig. 3 that the experimental behavior of $T_c/T_c(0)$ with volume change is not well reproduced. The linear behavior is not obtained for any of the calculated curves of Fig. 3. At this point it is necessary to mention that in order to reproduce the value of T_c at zero pressure, a very small and negative value of μ^* is required ($-0.001\,26$). This can be seen as a consequence of the small value of λ obtained in our calculation. When we use 0.1 for μ^*, we obtain for $T_c(p=0)$ a value of 0.015 K. Curve E in Fig. 3 corresponds to a value of T_c at zero pressure, $T_c(0)$ of 1.13 K, which is very close to the experimental value of $T_c(0)$, 1.19 K. For this reason we take curve E as our prediction of the variation of $T_c/T_c(0)$ with volume. We can see from this figure a deviation upwards from the linear relationship. This characteristic behavior is found in other calculations (see Refs. 28–32).

We should mention that our aim in this work is not a careful determination of the zero pressure T_c. If this were our purpose, we should have to take into account the electronic band structure. Our interest in this work is to predict changes in T_c. It is expected that the inclusion of the band structure is not the principal ingredient but rather changes in it, which probably have a relatively small effect.[20,30,32]

To our knowledge, no previous work has included first-principles calculations of all the relevant metallic properties at each volume. In Ref. 29 a first-principles calculation of the volume dependence of $T_c/T_c(0)$ is made. A pseudopotential proposed by Rasolt and Taylor[8] is used, but the same bare pseudopotential, rescreened, is used at all volumes.

In this work we have calculated the bare ion pseudopotential for each volume. We found that the change of the bare ion pseudopotential with volume is small. This can be seen in Fig. 4, where we show $q^2v(q)/(4\pi Z)$, where

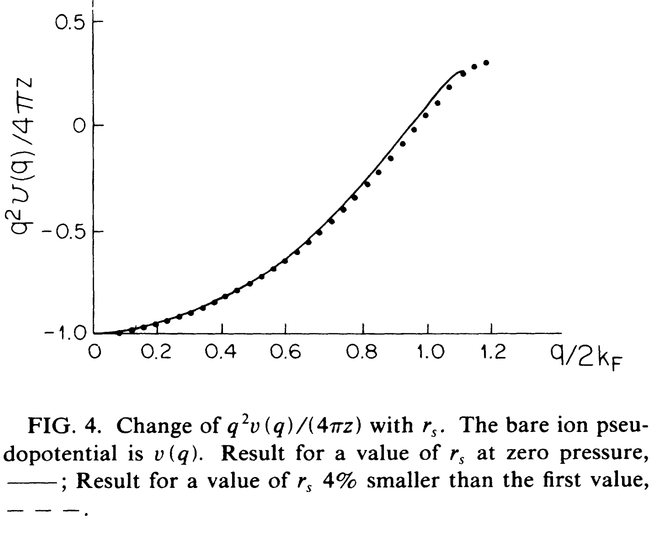

FIG. 4. Change of $q^2v(q)/(4\pi z)$ with r_s. The bare ion pseudopotential is $v(q)$. Result for a value of r_s at zero pressure, ——; Result for a value of r_s 4% smaller than the first value, — — —.

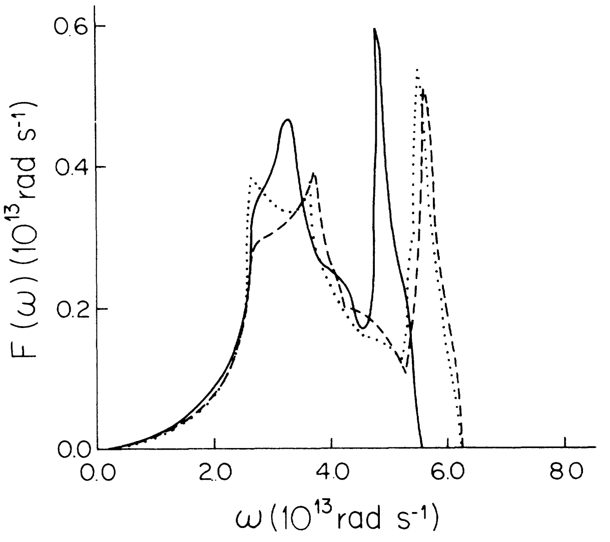

FIG. 5. Phonon density of states. The continuous curve is the result of this work. Measurements from Ref. (34), — — —; Born–Von Kárman fit from Ref. (35), · · · .

$v(q)$ is the bare ion pseudopotential, for two different values of r_s. The first is for zero pressure and the second for a value of r_s which is 4% smaller than the first value.

In Fig. 5 we show our calculated phonon density of states $F(w)$ at atmospheric pressure and compare it with two experimental results deduced from Born–Von Kárman fits to neutron measurements. The overall shape is very similar. Our maximum phonon frequency is 5.5×10^{13} rad/s, which corresponds to 8.75×10^{12} Hz indicated in Fig. 2. The experimental fit has a maximum phonon frequency corresponding to 6.1×10^{12} Hz. This gives a difference of 9.8% with respect to the experimental fit for this maximum phonon frequency.

For the rest of the values of r_s we have indications to believe that the phonons generated using our pseudopotentials for each volume are good. This is because the elastic constants as functions of pressure, calculated using our pseudopotentials are in good agreement with experiment for aluminum and lithium.[33] If we take our phonons as functions of pressure as good, we may look at μ^* like a parameter which may be responsible for the deviation upwards from the linear relationship. This parameter would have to change much more rapidly than what in general is believed it should vary with r_s. If μ^* changes like

$$\frac{\mu^*(\Delta r_s)}{\mu^*(0)} = 1-13.7(\Delta r_s)+29(\Delta r_s)^2 ,$$

where Δr_s is the percentage of change in Δr_s, the curve E in Fig. 3 would become the linear relationship between $T_c/T_c(0)$ and the volume given by the experimental results.

In any case, a careful study of changes in μ^* or band structure with r_s should be made to be incorporated in the calculation of the volume dependence of $T_c/T_c(0)$.

As a final comment we have that for aluminum, the difference between the values of T_c obtained using the formulas of McMillan and Leavens and solving the Eliashberg gap equations is of the order of ±0.02 K for each value of μ^*.[29]

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