Calculation of the pressure dependence of the superconducting transition temperature of aluminum

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The pressure dependence of the superconducting transition temperature of aluminum is studied by self-consistently calculating the phonon frequencies and the electron-phonon coupling as functions of volume. The rapid change in T_c with pressure in aluminum is reproduced well by the calculation.

The application of hydrostatic pressure rapidly depresses the superconducting transition temperature T_c of aluminum. It is reduced to 0.075 K at 62 kbar (corresponding to a volume change of about 7%) from its zero-pressure value of 1.18 K.[1] Furthermore, it appears that T_c varies linearly with volume at least in the pressure range measured. There have been several theoretical models addressing the problem of superconductivity under pressure,[2-7] and for aluminum, more recently, using rescreened pseudopotentials,[8] Whitmore[9] has calculated the volume dependence of T_c. In these models solutions of the Eliashberg equation for T_c give an upwards deviation from the measured relationship between T_c and the change in volume. To explain their experimental data Gubser and Webb[1] suggested a peculiar behavior for the electron-phonon interaction which would go through a maximum with pressure. However it appears unlikely that such a dependence would occur in aluminum without a structural change.

In the present work we use a recently developed method to calculate the $\mathbf{q}$ dependence of the electron-phonon coupling in metals.[10] This method does not use the rigid-ion approximation and it has the advantage that both the phonon frequencies and the McMillan parameter λ can be calculated *ab initio* using only the atomic number and atomic mass as inputs. By varying the volume of the unit cell, the pressure dependence of these quantities can easily be studied. We find that as the pressure increases, λ is suppressed by the rapid increase in the phonon frequencies. The suppression of λ is only slightly counteracted by the moderate increase in the electron-phonon matrix element. Using McMillan's[11] equation, the rapid decrease of T_c is accounted for without assuming any peculiar behavior to the electron-phonon interaction. But the linearlike behavior of the experimental data is not reproduced.

The $\mathbf{q}$-dependent λ, $\lambda_{\mathbf{q}}$, is defined for the monatomic case in terms of the usual electron-phonon matrix element,[12]

$$\lambda_{\mathbf{q}} \equiv \sum_{\nu} \lambda_{\mathbf{q}\nu} \equiv \sum_{\nu} 2N(E_F) \frac{\langle\langle |M_{\mathbf{q}\nu}(n\mathbf{k},n'\mathbf{k}')|^2 \rangle\rangle}{m\omega_{\mathbf{q}\nu}^2} , \quad (1)$$

where $N(E_F)$ is the density of states (DOS) per atom and per spin at the Fermi level E_F, m is the atomic mass, $\omega_{\mathbf{q}\nu}$ is the phonon frequency for wave vector $\mathbf{q}$ and branch ν, M is the scattering matrix element, and the symbol $\langle\langle\ \rangle\rangle$ denotes a Fermi surface average over states $\mathbf{k}$ and $\mathbf{k}'$ and bands n and n'.[10]

To evaluate the matrix elements and the phonon frequencies the electronic properties of the solid are needed. This is achieved by using an *ab initio* pseudopotential total-energy scheme.[13] This scheme gives both the structural properties[14] and the phonon frequencies by using two calculations with identical supercells[15] for the undistorted and the distorted crystal and by taking the difference in the total energies. In the harmonic approximation the square root of this difference is proportional to the phonon frequency,

$$\omega_{\mathbf{q}\nu} = \left(\frac{2\Delta E}{m\langle u^2 \rangle} \right)^{1/2} , \quad (2)$$

where $\langle u^2 \rangle$ is the mean square of the atomic displacements which depends on both $\mathbf{q}$ and ν. For a monatomic crystal, m is the atomic mass which also enters in Eq. (1).

Once the two potentials are self-consistently converged for both the undistorted crystal and a crystal distorted by a frozen phonon, the electron-phonon matrix element is calculated using the finite-difference method to compute the gradient of the potential with respect to the distortion.[10] The McMillan parameter λ can then be obtained from Eq. (1) by averaging the $\lambda_{\mathbf{q}}$'s in the Brillouin zone (BZ) as follows:

$$\lambda = \frac{1}{\Omega_{\mathrm{BZ}}} \int_{\mathrm{BZ}} \lambda_{\mathbf{q}} d^3q , \quad (3)$$

where Ω_{BZ} is the volume of the Brillouin zone.

Since the most important contribution to λ comes from the zone edge phonon and since we are mostly interested in the pressure dependence of the coupling, we have calculated only the phonons corresponding to a wave vector $\mathbf{q}$ at the Brillouin zone boundaries in two crystallographic directions, [100] and [111]. Six different volumes have

been considered starting from the theoretical equilibrium volume which is slightly smaller than the experimental value[14] (the equilibrium lattice constant a_0 is taken to be 4.013 instead of 4.02 Å experimentally). The pressure is then related to the volume through the Murnaghan's equation of states[16] using the calculated bulk modulus and its derivative with respect to pressure. The highest pressure considered here is 99.2 kbar which corresponds to a volume change of 10%.

The pressure variation of the frequencies also give the mode Grüneisen parameter γ_G by $-d\ln\omega/d\ln V$. The average of all these parameters over all the modes gives the Grüneisen parameter which is used to vary the Debye temperature Θ_D with pressure in the McMillan equation,

$$T_c=\frac{\Theta_D}{1.45}\exp\left[\frac{-1.04(1+\lambda)}{\lambda(1-0.62\mu^*)-\mu^*}\right]. \quad (4)$$

This equation is then used to calculate T_c and the first value of μ^* is fitted to reproduce the experimental T_c at zero pressure. The pressure variation of μ^* is taken from the empirical relation of Bennemann and Garland[17] with the use of the DOS at E_F and the pressure variation of this quantity,

$$\mu^*(P)=\mu^*(0)\frac{2N(E_F,P)[2N(E_F,0)+1]}{2N(E_F,0)[2N(E_F,P)+1]}, \quad (5)$$

where $N(E_F,P)$ is the DOS at E_F in states per eV and per spin, for a pressure P and $\mu^*(P)$ is the pressure-dependent μ^*. The pressure variation of μ^* is only about 1%, see Table II. All the other quantities in Eq. (3) are computed directly for different volumes.

In Fig. 1 the pressure variation of the scattering term

$$\langle\langle|M_{\mathbf{q}\nu}(n\mathbf{k},n'\mathbf{k}')|^2\rangle\rangle=\langle\langle|\langle\psi_{n\mathbf{k}}|\boldsymbol{\varepsilon}_{\mathbf{q}}\cdot\nabla V|\psi_{n'\mathbf{k}'}\rangle|^2\rangle\rangle \quad (6)$$

is plotted as a function of volume change for the longitudinal and transverse mode in the [100] direction and it is compared to the free-electron-gas results (FEG). The matrix elements increase with pressure more slowly than the FEG result. They generally increase with pressure because there is an explicit dependence on $1/V$. It should be noted that only the longitudinal mode can be usefully compared with the free-electron model results because the transverse mode includes umklapp processes which are not present in the FEG calculation.

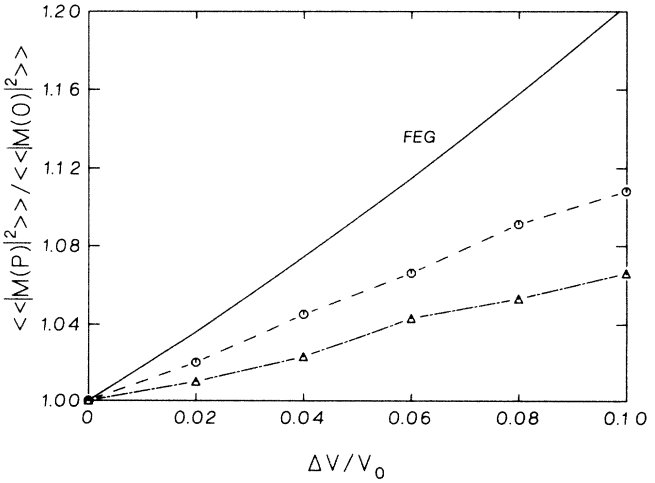

FIG. 1. Pressure variation as a function of volume change of the scattering term [Eq. (6)] for the free electron model (solid line), for the longitudinal [100] mode (circles), and the transverse [100] mode (triangles).

In Table I (a) and (b), the DOS at E_F, the phonon frequency, and $\lambda_{q\nu}$ are shown as a function of pressure for the [100] and [111] directions, respectively. In both cases the increase in the phonon frequencies dominates the behavior of λ, and λ decreases as the volume increases even though the scattering term increases. These results depend on the number of plane waves taken in the calculation of the potential and the total energy. The largest plane-wave energy E_{PW} chosen here is 10.0 Ry which corresponds to approximately 70 plane waves per atom. If a smaller E_{PW} is chosen the behavior with pressure is less pronounced both for the increase of the scattering term and for the phonon hardening. The mode Grüneisen parameters for an energy cutoff of 6.0 Ry are 1.7 and 2.9 for the longitudinal and transverse mode, respectively, in the [100] direction and 1.8 and 1.5 in the [111] direction. A direct average gives 1.9 which is the same as Whitmore[9] but somewhat lower than the experimental values which are about 2.2–2.6.[7,18–20] For a cutoff of 10.0 Ry the values are, respectively, 1.9, 3.0, 2.1, and 2.7 giving an average Grüneisen parameter of 2.4 which is closer to experiment than the less converged one.

In Table II the variation of T_c is shown together with all the quantities needed to compute T_c in the McMillan equation. The Coulomb repulsion μ^* at normal pressure is adjusted to obtain the experimental value of the transition temperature. Since the $\lambda_{\mathbf{q}}$'s are not calculated over the whole BZ, the average λ is not expected to give the experimental T_c without an adjusted μ^*. This average λ is calculated taking into account the sixfold symmetry of the

TABLE I. The computed quantities for the calculation of the electron-phonon coupling in the (a) [100] and (b) [111] directions. The DOS is given in states per Rydberg per spin, and the frequencies in 10^{13} rad/s.

$-\Delta V/V$	P (kbar)	$N(E_F)$	ω_L	λ_L	ω_T	λ_T	λ_q
			(a) [100] direction				
0.00	· · ·	2.69	6.33	0.1284	3.60	0.1086	0.3456
0.02	15.2	2.65	6.55	0.1205	3.80	0.0971	0.3147
0.04	32.4	2.61	6.79	0.1132	4.01	0.0868	0.2868
0.06	51.9	2.57	7.04	0.1058	4.23	0.0781	0.2620
0.08	74.0	2.53	7.28	0.0995	4.46	0.0699	0.2393
0.10	99.2	2.49	7.54	0.0928	4.68	0.0634	0.2196
			(b) [111] direction				
0.00	· · ·	2.72	6.09	0.1528	2.65	0.1070	0.3668
0.02	15.2	2.69	6.38	0.1428	2.78	0.0991	0.3410
0.04	32.4	2.66	6.68	0.1274	2.91	0.0922	0.3118
0.06	51.9	2.62	7.03	0.1155	3.03	0.0867	0.2889
0.08	74.0	2.59	7.30	0.1078	3.23	0.0785	0.2648
0.10	99.2	2.55	7.35	0.1055	3.43	0.0708	0.2471

TABLE II. The computed quantities entering the McMillan formula as functions of pressure.

$-\Delta V/V$	P (kbar)	Θ_D (K)	λ	μ^*	T_c (K)	$T_c/T_c(0)$
0.00	· · ·	428	0.3577	0.0836	1.18	1.00
0.02	15.2	449	0.3297	0.0834	0.74	0.63
0.04	32.4	472	0.3011	0.0833	0.40	0.34
0.06	51.9	497	0.2774	0.0831	0.21	0.18
0.08	74.0	523	0.2539	0.0828	0.09	0.08
0.10	99.2	551	0.2353	0.0826	0.04	0.03

[100] axis and the eightfold symmetry of the [111] axis. In order to compare these results with experiment they are plotted in Fig. 2 as a function of pressure where the squares are the points calculated in our model and the line represents the experimental results of Gubser and Webb.[1] The rapid decrease of T_c is well reproduced by the theory without assuming any peculiar behavior of the electron-phonon coupling. The main reason for the success of this calculation relative to previous attempts is attributed to the accurate calculation of the phonon frequencies under pressure. This coincides with Witmore's conclusion[9] about the failure of his model to fully account for this rapid decrease of T_c. The fact that this calculation is carried out to self-consistency for each volume allows the variation of the phonon frequencies with pressure to be closer to the experimental one.

On the other hand, the linear dependence of T_c on the volume change is not reproduced by this theory. Two possible sources of uncertainty in the theory can arise in the treatment of μ^* and the equation for T_c. For example, μ^* and its presure dependence are treated only in an approximate way, and the coefficients used in the McMillan equation could be pressure dependent. However, all the theoretical models including this one predict a saturation of T_c rather than the linear dependence. It would be interesting to obtain measurements of T_c at high pressure to investigate this difference.

These results and those obtained previously on primitive hexagonal silicon[21] show that it is now possible to study the pressure dependence of the superconducting transition temperature to a high degree of accuracy from first principles. The electron-phonon couplings and the phonon frequencies are well described by the total-energy frozen-phonon method. One of the remaining challenges is to compute the Coulomb repulsion μ^* from first principles.

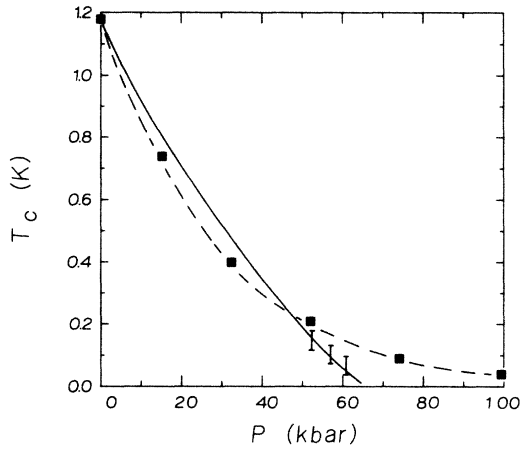

FIG. 2. The theoretical superconducting transition temperature (squares) as a function of pressure compared to the experimental results of Gubser and Webb (Ref. 1) (solid line). The dotted line between the calculated points is only a guide for the eyes.

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