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## High-Pressure Effects on the Superconducting Transition Temperature of Aluminum

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The superconducting transition temperature  $T_c$  of aluminum has been measured as a function of pressure to 62 kbar, at which point  $T_c$  was reduced to 0.075 K from its zero pressure value of 1.18 K. These data cover ranges of temperature and pressure which allow differentiation between theoretical and empirical predictions. The data clearly obey the empirical relation of Smith and Chu and suggest a new volume dependence for the electron-phonon interaction.

Several theoretical models<sup>1-10</sup> have been proposed to explain the effects of hydrostatic pressure  $P$  on the superconducting transition temperature  $T_c$  of nontransition metal superconductors. Calculations of  $T_c(P)$  have been reasonably successful in explaining the reduction of  $T_c$  at low pressures (0 to 20 kbar); however, the effects of higher pressures remain uncertain. Smith and Chu<sup>11</sup> proposed an empirical relation which described the pressure effects of  $T_c$  up to 20 kbar and suggested its validity at even higher pressures. The relation is

$$\Delta T_c / T_0 = \alpha \Delta V / V_0, \quad (1)$$

where  $T_0$  is the zero-pressure transition temperature,  $V_0$  is the zero-pressure atomic volume,  $\Delta V$  is the change in volume induced by hydrostatic pressure, and  $\alpha$  is a material-dependent constant. None of the theoretical models describing the volume (pressure) effects on  $T_c$  predict a volume dependence of this form at pressures over 20 kbar.

In this Letter we report the results of our study on the pressure dependence of  $T_c$  in aluminum. The data cover ranges of temperature and pressure which for the first time allow differentiation between the various theoretical and empirical predictions. The transition temperature of Al was reduced to less than  $\frac{1}{10}$  of its zero-pressure value ( $T_0 = 1.18$  K) at a pressure of 62 kbar which represents the largest pressure-induced percentage reduction in  $T_c$  ever reported.

Details of the pressure cryostat for achieving the required temperatures and pressures are described elsewhere<sup>12</sup> but are briefly reviewed here

since it has some unique features. Figure 1 shows a cross-section drawing of the pressure cell used for achieving  $P \leq 100$  kbar and  $T \geq 0.025$  K. A 0.1-mm-diam Al sample is contained in a hardened BeCu gasket and positioned between two diamond anvils each having 0.5-mm faces. Pressure produced between these anvils is controlled hydraulically by externally regulating the <sup>4</sup>He fluid pressure in a large bellows which drives a piston holding the top diamond. This feature permits acquisition of data over the entire pressure span in one run. Sample pressures are proportional to the externally measured <sup>4</sup>He pressures. The system was calibrated against published Al data up to 20 kbar.<sup>13</sup>

The BeCu pressure cell is an integral part of a dilution refrigerator. The top plate of the cell contains a small annular cavity which is the mix-

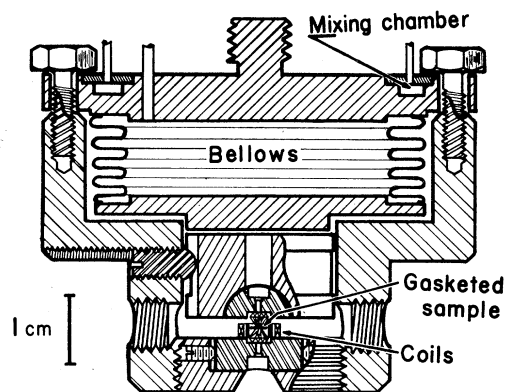


FIG. 1. Cross section of the variable-pressure, low-temperature, diamond-anvil cell.

ing chamber of the dilution refrigerator; thus, the entire pressure cell is cooled to low temperatures. Temperatures were measured with a calibrated germanium resistance thermometer attached to the walls of the pressure cell.

The transition temperature of the sample was determined by observing the change in magnetic moment of the sample as it went from the normal to the superconducting state in the presence of a small magnetic field. Changes in moment produce magnetic flux variations inside a superconducting coil surrounding the sample which, in turn, are detected by a commercial superconducting-quantum-interference-device (SQUID) magnetometer<sup>14</sup> located in the outer <sup>4</sup>He bath. The magnetometer output is proportional to the sample volume  $v$  and is given by

$$\Delta\Phi = Hv/2r_c(1 - D), \quad (2)$$

where  $\Delta\Phi$  is the flux change,  $H$  is the ambient magnetic field,  $r_c$  is the coil radius, and  $D$  is the demagnetization factor. Magnetometer outputs corresponding to flux changes of approximately  $10^{-7}$  G cm<sup>2</sup> were observed when the sample expelled Earth's magnetic field of 0.3 Oe. Incomplete flux expulsion, indicative of sample inhomogeneities or pressure gradients, would produce a profound reduction in signal strength and was not observed.

Figure 2 shows the experimental transition-temperature data as a function of pressure obtained in the manner just described. The vertical lines representing the data are indicative of the width of the transition. The width did not increase at high pressures which again supports our contention that large pressure gradients were not present in the Al sample. Half of the width is attributed to demagnetization effects.

The solid line in Fig. 2 is the empirical relation of Smith and Chu, Eq. (1), where the volume dependence has been converted to pressure dependence using Bridgman's room-temperature compressibility data.<sup>15</sup> No deviations from this relation are observed although the data extend well into the range where deviations had been theoretically predicted.

Effects of volume (pressure) on  $T_c$  can be calculated using the formalism developed by McMillan.<sup>16</sup>

$$T_c = \frac{\theta_D}{1.45} \exp\left\{\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right\}, \quad (3)$$

where  $\theta_D$  is the Debye temperature,  $\lambda$  is the electron-phonon interaction parameter, and  $\mu^*$  is

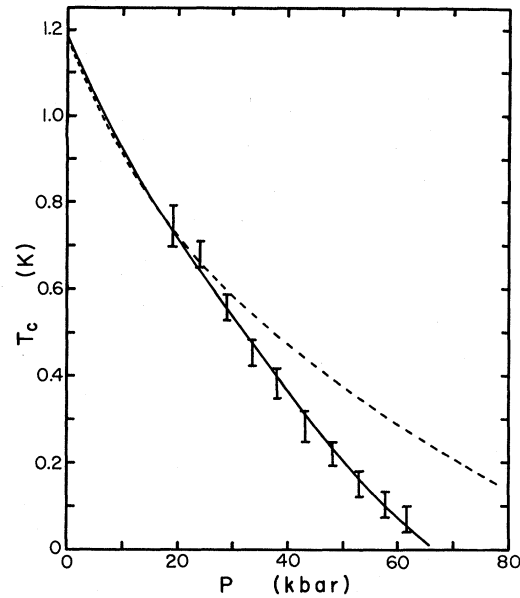


FIG. 2. Effect of pressure on the superconducting critical temperature of aluminum. Bars indicate the width of the observed transitions. The solid line is the empirical relation of Smith and Chu (Ref. 11). The dashed line is the result of the volume-dependent McMillan expression [Eq. (7)] with  $\theta_D^0 = 428$  K,  $\gamma_G = 2.2$ ,  $\lambda_0 = 0.47$ ,  $\mu^* = 0.15$ , and  $\varphi = 2.8$ .

the Coulomb repulsion term. The volume dependence of  $\theta_D$  is described by Grüneisen theory.<sup>17</sup> The volume dependence of  $\mu^*$  is small<sup>3</sup> and has generally been ignored. Calculation of volume (pressure) effects on  $T_c$  thus revolves around the calculation of  $\lambda$  as a function of volume.

The electron-phonon coupling constant is given by the expression<sup>16</sup>

$$\lambda = N(0)\langle I^2 \rangle / M\langle \omega^2 \rangle, \quad (4)$$

where  $N(0)$  is the electronic-band-structure density of states at the Fermi energy,  $\langle I^2 \rangle$  is an average of the electron-phonon matrix element over the Fermi surface,  $M$  is the atomic mass, and  $\langle \omega^2 \rangle$  is a weighted average of the square of the phonon frequency. Pseudopotential methods have been successful in calculating  $\lambda_0$ , the zero-pressure electron-phonon constant, for nontransition metals where accurate phonon dispersion curves are known and where pseudopotential form factors have been reliably determined by comparison with Fermi-surface data.<sup>18,19</sup> Extension of these calculations to higher pressures involves approximations as to the pressure dependence of phonon frequencies and of the pseudopotential form factors. Such calculations have been done

for aluminum and lead, in particular, by a number of authors<sup>3,6,8,10</sup> and adequately describe the low-pressure experimental data. All of these calculations, however, show substantial upward deviations from the empirical Eq. (1) at pressures over 25 kbar.

Since our data verify Eq. (1) at these higher pressures a re-examination of the approximations used to extend pseudopotential theory to higher pressures is needed. Taking the logarithmic derivative of Eq. (4) with respect to volume, one has

$$\frac{\partial \ln \lambda}{\partial \ln V} = \frac{\partial \ln [N(0)\langle I^2 \rangle]}{\partial \ln V} + \frac{\partial \ln [1/\langle \omega^2 \rangle]}{\partial \ln V}. \quad (5)$$

Ott and Sorbello<sup>10</sup> have shown that at least for small volume changes the first term in Eq. (5) is equal to a negative constant  $S$ , while the last term is approximately given by twice the room-temperature Grüneisen parameter,  $\gamma_G$ . The volume dependence of  $\lambda$  is therefore given by

$$\frac{\partial \ln \lambda}{\partial \ln V} = S + 2\gamma_G \equiv \varphi. \quad (6)$$

The volume-dependent expression for  $T_c$  is thus

$$T_c = \frac{\theta_D^0 (V/V_0)^{-\gamma_G}}{1.45} \exp \left\{ \frac{-1.04 [1 + \lambda_0 (V/V_0)^\varphi]}{\lambda_0 (V/V_0)^\varphi - \mu^* [1 + 0.62 \lambda_0 (V/V_0)^\varphi]} \right\}, \quad (7)$$

where  $\theta_D^0$  is the zero-pressure Debye temperature. Equation (7) is shown by the dashed line in Fig. 2 using the zero-pressure Al data given in the caption. Note that substantial differences between this equation and the experimental data [and Eq. (1)] become apparent at pressures in excess of 25 kbar.

A possible explanation for the inadequacy of Eq. (7) is in the approximations used in deriving

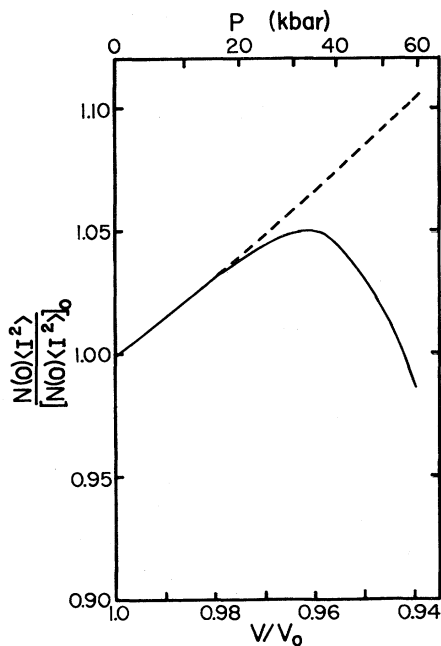


FIG. 3. The normalized volume dependence of  $N(0)\langle I^2 \rangle$ . The dashed line gives the dependence assumed in deriving Eq. (7). The solid line shows the dependence required to fit the observed data.

the volume dependence of  $\lambda$  or, more precisely, the volume dependence of  $N(0)\langle I^2 \rangle$ . The assumed volume dependence of  $N(0)\langle I^2 \rangle$  is shown in Fig. 3 as a dashed line. To bring theory into agreement with experiment it is necessary to assume a different volume dependence as shown by the solid line in Fig. 3.  $N(0)\langle I^2 \rangle$  increases as expected to a maximum value at 35 kbar where it is about 5% greater than its zero-pressure value and then begins to decrease rapidly at higher pressures.

A volume-dependent  $\mu^*$  could explain the data; however, it would have to increase from 0.15 at zero pressure to 0.20 at 60 kbar in order to remove the discrepancy solely in terms of  $\mu^*$ . Such a large volume dependence seems unlikely, although it cannot be ruled out at the present time. Incorporation of pressure variations in  $\gamma_G$  increase the discrepancy between theory and experiment. Refined pseudopotential calculations which eliminate or modify the various approximations used in the calculation of  $\lambda$  are therefore needed to understand these high-pressure data and to explain the empirical relation of Eq. (1).

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## Core-Electron Excitation Spectra of Si, SiO, and SiO<sub>2</sub> †

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The excitation spectra of Si(2*p*) and O(1*s*) core electrons, measured by low-energy electron-loss spectroscopy, yield detailed information on the excited states of Si, SiO, and SiO<sub>2</sub>. The presence of an empty surface state near the top of the valence band on clean Si is directly demonstrated for the first time. For SiO<sub>2</sub>, the results indicate the presence of five empty states in the conduction band.

The study of the electronic valence states of solids by either photoemission, including electron spectroscopy for chemical analysis, or x-ray emission has been of considerable interest in recent years. Complementary experiments to probe the spectrum of excited electronic states have generally been limited to valence band excitations which require some form of deconvolution to isolate the desired spectrum. This problem may be overcome by measuring the core-level excitation spectrum with a tunable x-ray source, such as synchrotron radiation.<sup>1</sup> It was recently demonstrated<sup>2,3</sup> that excited states of semiconductors may also be conveniently studied by low-energy electron loss spectroscopy (LEELS) involving excitations from relatively shallow *d*-core states into both bulk and surface-related final states in GaAs and Ge. We have extended these measurements and report here for the first time detailed excitation spectra of deep core electrons of binding energies  $\geq 100$  eV. In particular we report excitation spectra for Si(2*p*) and O(1*s*) core levels. The results give new insights on surface-related structure in Si and the elec-

tron excitation scheme of SiO<sub>2</sub>, a material of considerable technological interest.

The loss spectra were measured in the reflection mode with a cylindrical-mirror analyzer. The second derivatives of the spectra were measured to enhance detail with an estimated energy resolution of 0.5 eV. The experimental details have been reported elsewhere.<sup>2,3</sup> The silicon wafers, *n* type with  $\rho \sim 1 \Omega \text{ cm}$ , were cleaned by Ar<sup>+</sup> ion bombardment and annealed so that the appropriate surface reconstructions, 7×7 for (111) and 2×1 for (100) surfaces, were observed by electron diffraction. The oxygen coverage was measured by Auger-electron spectroscopy and assumes a room-temperature saturation coverage of one monolayer.<sup>4</sup>

The loss spectra due to excitations out of the Si(2*p*) core level for clean and variously oxidized silicon surfaces are shown in Fig. 1. The spectra for (100) and (111) surfaces are similar and we arbitrarily illustrate results for only the (100) surface. The loss spectrum of the clean Si(100)2×1 surface is shown as a solid line in Fig. 1(a). This strong loss peak at 98.7 eV is very sensi-