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Negative thermal expansion of MgB_2 in the superconducting state and anomalous behavior of the bulk Grüneisen function

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The thermal expansion coefficient α of MgB_2 is revealed to change from positive to negative on cooling through the superconducting transition temperature T_c. The Grüneisen function also becomes negative at T_c followed by a dramatic increase to large positive values at low temperature. The results suggest anomalous coupling between superconducting electrons and low-energy phonons.

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Superconductivity in the binary compound MgB_2 near 39 K is a fascinating development. Over the last few years, scientists have argued that a lattice instability[1] and/or anomalous phonon behavior[2] might be responsible for the high transition temperature. Specific attention has focused on the E_{2g} phonon, a bond-stretching phonon within the plane of the hexagonal crystal structure.[2–4] In-plane tensile strain, induced by lattice mismatch through thin-film growth, increases the superconducting transition temperature T_c to 41.8 K; this enhancement was attributed to a decrease in the E_{2g} phonon frequency.[5] Phonons can be studied with techniques such as Raman spectroscopy[3,4] and heat capacity.[6–8] Often neglected in the study of phonons is thermal expansion, partly because of the exceptional resolution needed to resolve the transition at T_c.

Thermal expansion from powder diffraction measurements[9,10] of MgB_2 have revealed an anomalous volume expansion on cooling below T_c. However, *high-resolution* thermal expansion measurements (dilatometry) with a relative sensitivity approximately four orders of magnitude better than powder diffraction are required for meaningful thermodynamic analysis. Such measurements of polycrystalline MgB_2 were reported,[11] but discrepancies with the diffraction data, such as the temperature at which the thermal expansion coefficient α changes from positive to negative, are apparent.

In this Rapid Communication, high-resolution thermal expansion measurements of polycrystalline MgB_2 are presented. The results reveal a change in sign of α at T_c, with negative thermal expansion below T_c; these data agree with diffraction investigations,[9,10] but offer *exceedingly* greater detail. Analysis of the bulk Grüneisen function reveals anomalous behavior due to dominant low-energy phonon modes. The change in sign of α at *precisely* T_c suggests a connection between these phonon modes and superconductivity.

MgB_2, synthesized with ^{11}B as described previously,[12] was pelletized (diameter=4.6 mm), placed in a boron nitride crucible and heated to 800 °C for 30 min at 3 GPa using a cubic multianvil press. A very thin black layer, impurities from surface reaction with boron nitride, was removed, leaving behind a brilliant gold-colored MgB_2 sample with density 2.56 g/cm^3 (100% of theoretical density). Heat capacity was measured with a thermal-relaxation technique. T_c versus pressure was determined inductively (0.12 Oe rms field at 1023 Hz) to 0.63 GPa using a helium pressure medium; a manganin sensor at room temperature served as a manometer.[13]

Thermal expansion was measured with a capacitive dilatometer cell (Fig. 1) constructed from fused quartz,[14] which has among the smallest known thermal expansions.[15] Calibration is realized by measuring copper[16] at 300 K and 79.3 K, where the length change of fused quartz, $\Delta L/L_{300K}$, is zero.[15] During measurements, the sample and cell (in thermal equilibrium) are warmed at 0.2 K/min as capacitance and temperature are recorded at intervals ranging from 0.1 to 0.2 K. The data are corrected for temperature-dependent changes in capacitance of the empty cell, measured in a separate experiment, and the differential expansion

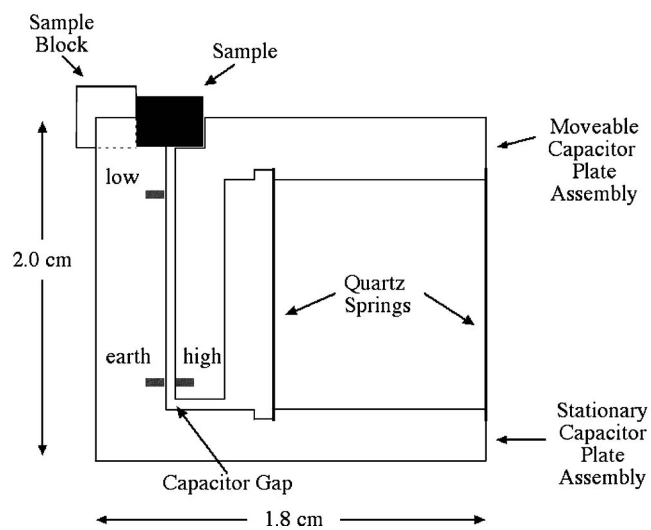

FIG. 1. Composed of two L-shaped pieces connected via 100 -μm-thick springs, *all* components of the dilatometer cell are made of fused quartz. Cr/Au (100 Å/1000 Å) 1.6 cm^2 capacitor plates are perpendicular to the page's plane (electrical contacts shown); a guard ring (at earth) encircles the low plate. A Be-Cu strap (not shown) secures the sample block. Expansion of the sample changes the capacitor gap.

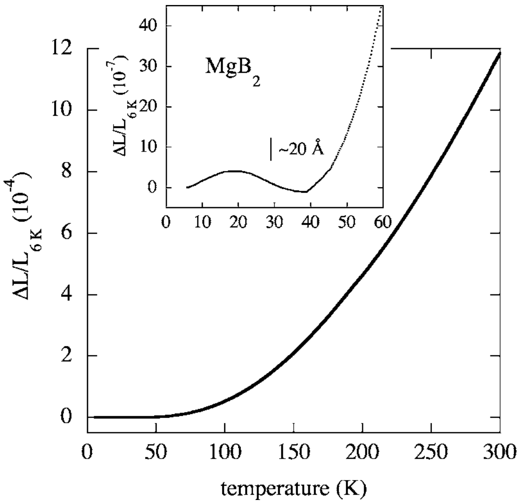

FIG. 2. Linear thermal expansion $\Delta L/L_{6K}$ of the 4238 μm long specimen. The region near T_c is shown in the inset; the 20 Å scale indicates the absolute length change.

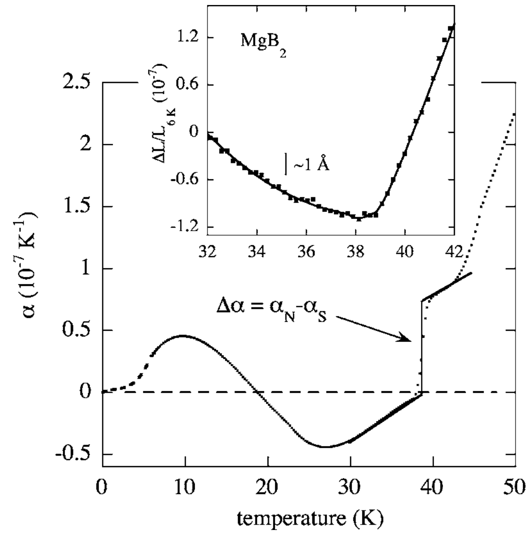

FIG. 3. Inset shows $\Delta L/L_{6K}$ near T_c illustrating the change in slope, excellent resolution of the data, and continuous nature of the phase transition. The solid line in the inset is the fit that, after differentiation, yields the thermal expansion coefficient α (main panel). Solid lines indicate the jump in α at T_c. The dashed line below 6 K denotes hypothetical behavior.

between the cell and sample using data for quartz.[15] These contributions amount to 2.7% and 4.1%, respectively, of the capacitance change due to the thermal expansion of MgB_2 over the temperature range 6 K $<T<$ 300 K; the latter correction would be 63 times larger if a conventional copper dilatometer cell were used to measure MgB_2, because of copper's large thermal expansion.[16] The specimen was measured along two perpendicular axes (4238 μm and 3665 μm long) to search for preferred crystallographic orientation effects (none were detected).

Linear thermal expansion $\Delta L/L_{6K}$ is shown in Fig. 2. These raw data have been corrected for the thermal expansion of quartz as described above with no other processing. The length decreases with temperature, as occurs in most materials, but it expands on cooling below T_c=38.7 K as illustrated in the inset where the 20 Å scale reveals the *absolute* length change of the 4238 μm long specimen. The distinct change in $\Delta L/L_{6K}$ near T_c is highlighted further in the inset of Fig. 3 where *angstrom-scale* resolution and the continuous (second-order) nature of the phase transition are evident. The measurement was repeated three times along the 3665 μm length and three times along the 4238 μm length with similar results to those shown in Figs. 2 and 3. The overall linear expansion $(L_{300K}-L_{6K})/L_{6K}=119.2(4)\times 10^{-5}$.

The thermal expansion coefficient $\alpha=(1/L_{6K})\partial\Delta L/\partial T$ is obtained by fitting the data in Fig. 2 using Chebyshev polynomials and differentiating; overlap between neighboring fit regions assures a smooth derivative and caution is exercised near the sharp feature at T_c. This method is typical for taking derivatives when tiny changes between neighboring data points occurs.[17] The resulting α values are plotted between 0 and 50 K in Fig. 3; all six measurements showed similar behavior. Note that α(50 K) is 16.7 times smaller than that of copper,[16] a consequence of the large Debye temperature[7] of MgB_2. Negative thermal expansion sets in at precisely T_c and further inspection reveals a crossover at 18.7 K to $\alpha>0$. Furthermore, a broad peak is evident in α at 9.7 K, below which it decreases. According to the third law of thermodynamics, α should approach zero at T=0; this behavior is illustrated by the (hypothetical) dashed line in Fig. 3.

The jump in α at T_c (solid lines Fig. 3), $\Delta\alpha=\alpha_N-\alpha_S=6.3(7)\times 10^{-8}$ K^{-1}, was obtained after averaging the jumps observed in six measurements; N represents the normal state and S the superconducting state. This value agrees with $\Delta\alpha=5.8\times 10^{-8}$ K^{-1} reported previously;[11] in that paper, $\alpha<0$ below 10 K, but remained above zero for $T>10$ K. These differences may be associated with (1) the high density of our specimen, since polycrystalline MgB_2 prepared by the method in Ref. 11 is highly porous with low cohesiveness and elastic modulus,[18] (2) the higher T_c (38.7 K vs 37.8 K), or (3) the copper thermal expansion cell used in Ref. 11 which requires a significantly larger correction to the data than our cell (see above). Behavior in $\Delta L/L_{6K}$ similar to that of Fig. 2 was revealed in diffraction measurements,[9,10] but the present data offer far more resolution.

Heat capacity at constant pressure C_P was measured on the same sample. A background of the form $C_P=A_1T+A_3T^3+A_5T^5$ (A_1, A_3, and A_5 are constants) is subtracted, which was obtained by fitting C_P(9 tesla) in the range 25 K $<T<$ 50 K; the form of this background is identical to that used previously.[7] A clear feature is observed at T_c=38.7 K (lower inset of Fig. 4). The solid lines denote the steplike behavior expected for a continuous (second-order) phase transition. Using an entropy-conserving construction, the jump $\Delta C_P=-121(1)$ mJ/mole K is estimated.

The Ehrenfest relation,

$$\frac{dT_c}{dP}=3vT_c\frac{\Delta\alpha}{\Delta C_P}, \qquad (1)$$

provides the connection between the pressure derivative of T_c, $\Delta\alpha$, and ΔC_P (v is the molar volume). It has yielded

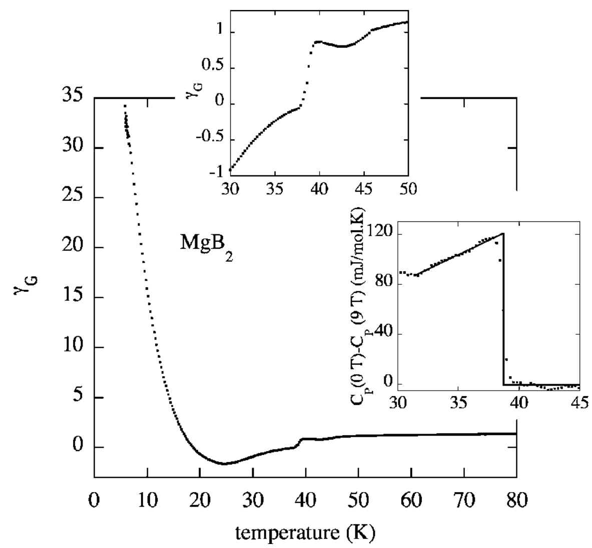

FIG. 4. The main panel and upper inset show the bulk Grüneisen function γ_G versus temperature. The lower inset shows heat capacity C_P after subtraction of C_P(9 tesla); the solid line indicates the jump expected for a continuous (second-order) phase transition.

dT_c/dP in agreement with experiment for other superconductors.[19,20] Using $\Delta\alpha=6.3(7)\times10^{-8}$ K^{-1}, $\Delta C_P=-121(1)$ mJ/mole K, and $v=1.74\times10^{-5}$ m^3/mole,[9] $dT_c/dP=-1.05(13)$ K/GPa is obtained. Variation in ΔC_P values[8] (66 mJ/mole K to 133 mJ/mole K) underscores the importance of measuring ΔC_P and $\Delta\alpha$ on the same sample to reliably estimate dT_c/dP.

To test the calculation via Eq. (1), dT_c/dP was measured on our sample using a *purely hydrostatic method*. Pressure was changed below 55 K and only one transition ($P=0.63$ GPa) was measured in solid helium. $T_c(P)$ was determined from the midpoint of the superconducting transition in the real part of the ac magnetic susceptibility. The data (Fig. 5) show that T_c decreases at $dT_c/dP=-1.07(0.03)$ K/GPa, similar to prior reports.[13] This value is in excellent agreement with the value predicted by

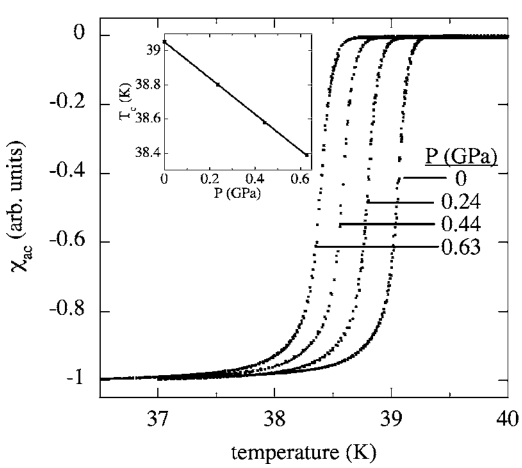

FIG. 5. In the inset T_c versus pressure is plotted. These data were determined from the midpoint of the transition in the ac magnetic susceptibility χ_{ac}, shown in the main panel.

the Ehrenfest relation. This observation together with the continuous behavior of $\Delta L/L_{6K}$ eliminates the possibility of a significant lattice instability in MgB_2 for 6 K$<T<$300 K.

While negative thermal expansivities are not that unusual,[21] the crossover of α from positive to negative, at precisely T_c, is rare. Tantalum exhibits a slight negative[22] α below T_c=4.4 K; what distinguishes this feature in MgB_2 is that α is eight times larger above T_c, and that it becomes strongly negative below T_c. Thus, the electronic transition into the superconducting state has a significant impact on the thermal expansion at and below T_c as revealed in Figs. 2 and 3.

Thermal expansion is a sensitive probe of phonon behavior which is analyzed through the bulk Grüneisen function $\gamma_G=\beta BV/C_V$ calculated using data[18] for the bulk modulus B and our measurements of the volume thermal expansion coefficient $\beta=3\alpha$, V, and C_P [the heat capacity at constant volume $C_V\approx C_P$ (Ref. 23)]. It is a dimensionless weighted sum[21] of γ_i values (i.e., $\gamma_G=\Sigma_i c_i\gamma_i/\Sigma_i c_i$ where $c_i=e^{-\hbar\omega_i/k_BT}$; $\hbar$ is the Planck constant divided by 2π and k_B is the Boltzmann constant) each associated with a phonon mode of vibrational frequency ω_i and $\gamma_i=-d\ln\omega_i/d\ln V$. γ_G has a value of 1.30 near 300 K, rises slightly to 1.35 at 90 K followed by a gradual decrease. This decrease continues (see Fig. 4), until γ_G crosses zero at T_c, reaches a minimum of -1.65 at 24.5 K, before increasing to 34.2 at 5.8 K. Nonmonotonic behavior of the Grüneisen function is a consequence of strong anharmonic lattice vibrations,[24] which have been observed[3,4] in MgB_2. The negative as well as the large positive values of γ_G must be associated with anomalous phonon modes that dominate the weighted sum due to their respective thermal populations; electron-phonon interactions will also play a role.

In other layered materials, negative α values are generally associated with transverse acoustic vibrations, which propagate in the layers,[24] leading to negative a-axis γ_i values. As a result, the change in sign of α and γ_G at T_c, coincident with hardening of the E_{2g} phonon,[4] is likely connected to planar electron-phonon interactions associated with the σ-band (in-plane) superconducting gap.[25–27]

At low temperature, differences in the intralayer bonding (along the c axis) may lead to low-energy phonon excitations and large c-axis γ_i values with high relative thermal population that cause the upturn of γ_G below 20 K; such behavior occurs in other layered materials, albeit with significantly smaller values[24] of γ_G. In MgB_2, the spectacular increase of γ_G coincides with a reduced C_P below $\approx$11 K, attributed to a second superconducting gap.[6,7] Thus, C_P is diminished because of electronic effects due to the second gap, α remains large, and their ratio leads to anomalously large γ_G values. These combined considerations suggest that the increase in γ_G at low temperature may result from out-of-plane electron-phonon interactions, associated with the weaker π-band superconducting gap,[25–27] which have a strong impact on the c-axis γ_i values.

The results presented here compliment spectroscopic phonon probes, some of which may be surface sensitive, by illustrating unusual phonon behavior in two fundamental *bulk* thermodynamic quantities, the Grüneisen function and the thermal expansion coefficient. Thermal excitations of electrons across the two superconducting gaps, and their coupling to low-energy lattice vibrations, play a role in the anomalous behavior of γ_G and α.

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