Pressure-Induced Superconductivity in CaLi$_2$

T. Matsuoka,* M. Debessai, J. J. Hamlin, A. K. Gangopadhyay, and J. S. Schilling

Department of Physics, Washington University, CB 1105, One Brookings Drive, St. Louis, Missouri 63130, USA

K. Shimizu

*KYOKUGEN, Center for Quantum Science and Technology under Extreme Conditions, Osaka University,
1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan*
(Received 20 February 2008; published 16 May 2008)

A search for superconductivity has been carried out on the hexagonal polymorph of Laves-phase CaLi$_2$, a compound for which Feng, Ashcroft, and Hoffmann predict highly anomalous behavior under pressure. No superconductivity is observed above 1.10 K at ambient pressure. However, high-pressure ac susceptibility and electrical resistivity studies to 81 GPa reveal bulk superconductivity in CaLi$_2$ at temperatures as high as 13 K. The normal-state resistivity displays a dramatic increase with pressure.

Li and Ca are both "simple" metals with one ($1s$) and two ($2s$) conduction electrons per atom, respectively. Recently, Tuoriniemi *et al.* [1] reported superconductivity in Li at extremely low temperatures ($T_c \approx 0.4$ mK). If Li is subjected to increasing pressure, a superconducting transition abruptly appears at $T_c \approx 5$ K for 20 GPa and climbs steeply, passing through a maximum at $14-20$ K for 30 GPa [2–4]. In addition, the electrical resistivity of Li increases sharply with pressure [2,5]. These results are in agreement with the prediction of Neaton and Ashcroft [6] that Li's electronic properties should become highly anomalous at extreme pressures. On the other hand, Ca is not known to superconduct at ambient pressure, but becomes superconducting at ~1.2 K under 50 GPa [7], reaching 25 K at 160 GPa (1.6 Mbar) [8], a record value of T_c for an elemental superconductor. The electrical resistivity of Ca also increases strongly with pressure [8]. It is notable that at these extreme pressures the conduction bandwidths in Li [6], Na [9], and Ca [10] are calculated to *decrease* under pressure, a counterintuitive result.

Recently, Feng *et al.* [11] pose the interesting question whether the anomalous properties predicted and found for Li and Ca under pressure carry over to the only known binary compound containing these two elements, the Laves-phase CaLi$_2$. Detailed electronic structure calculations by these authors for both hexagonal and cubic polymorphs of CaLi$_2$ lead them to predict that "the elevated density of states at the Fermi level, coupled with the expected high dynamical scale of Li as well as the possibility of favorable interlayer phonons, points to potential superconductivity of CaLi$_2$ under pressure." As for Li and Ca, the conduction bandwidth is predicted to decrease under high compression, narrowing at 139 GPa to only one-third the free-electron value [11]. The anomalous electronic properties in Li, Ca, and CaLi$_2$ under extreme pressures arise from the fact that as the ionic cores of the constituent elements approach each other and begin to overlap, the conduction electrons, which are excluded

from these ion cores, forfeit their nearly-free-electron character as they are forced into cramped, low-symmetry interstitial sites [6,9,11]. These arguments are quite general and should apply to a wide range of nominally free-electron elements, alloys, and compounds [9]. Since CaLi$_2$ serves as a test case for these ideas, high-pressure measurements on this material are of particular importance. To our knowledge, CaLi$_2$ has not yet been tested for superconductivity at any pressure, ambient or otherwise.

In this Letter we report measurements of the temperature-dependent electrical resistivity and ac susceptibility of hexagonal CaLi$_2$ at both ambient and high pressure to 81 GPa in a diamond-anvil cell (DAC). At ambient pressure no superconductivity is found above 1.10 K. For pressures above 11 GPa a superconducting transition is observed in both the electrical resistivity and ac susceptibility where T_c increases with pressure and passes through a maximum at 11–13 K near 40 GPa. In the normal state the electrical resistivity shows a remarkably large increase with pressure over the measured temperature range 2–300 K.

The starting materials for the synthesis of CaLi$_2$ are pieces of 99.98% Ca from Alfa Aesar and 99.99% Li rod from ESPI Metals. The first CaLi$_2$ sample (sample *A*) was prepared by melting together stoichiometric amounts of Ca and Li in a stainless steel crucible placed on a hot plate in an Ar-gas glove box. A 13 μm thick Ta foil was placed under the sample in the crucible and a thin Ta strip was used to stir the molten sample for approximately 30 min at a temperature somewhat above the melting temperature (235 °C) of CaLi$_2$. The residual resistivity ratio was found to be $\rho(300 \text{ K})/\rho(2 \text{ K}) \simeq 170$, a relatively high value for an intermetallic compound, which speaks for its phase purity. A second CaLi$_2$ sample (sample *B*) was prepared as sample *A*, but was then wrapped in a Ta foil, sealed in a quartz tube filled with Ar, and annealed for 24 h in a box furnace at a temperature slightly below the melting tem-

perature. Scanning electron microscopy (Hitachi S-4500) revealed the presence of a small amount of impurity phase (< 5 vol%) in sample *A*. The annealing procedure significantly reduced the amount of impurity phase in sample *B* to below 1 vol%.

In preparation for x-ray powder diffraction studies, an agate mortar and pestle in the Ar glove box was used to grind the brittle $CaLi_2$ sample to a powder which was filled together with a Si marker into glass capillary tubes (0.9 mm O.D. × 0.01 mm wall) and sealed shut under Ar gas. Five such capillary tubes were placed in a Rigaku Geigerflex D/max-B x-ray diffractometer utilizing Cu-K_α radiation. The powder diffraction pattern of both samples indicates single-phase material and confirms the hexagonal unit cell with $a = 6.293(1)$ Å and $c = 10.236(1)$ Å for sample *A* and $a = 6.287(1)$ Å and $c = 10.233(1)$ Å for sample *B*, in reasonable agreement with published values $a = 6.2899(5)$ Å and $c = 10.268(1)$ Å [12]. To search for possible impurity phases of unreacted Li or Ca, high resolution x-ray diffraction studies were carried out on sample *B* for those strong diffraction peaks with indices for Li (110) and for Ca (200), (220), and (311) which are well separated from the peaks of $CaLi_2$. Using the above diffractometer, no trace of any of these diffraction peaks could be detected within experimental resolution; this allows the estimate that the crystalline impurity concentration is below 1.7% for Li and 0.3% for Ca. From very high resolution synchrotron radiation studies on this sample, the estimate of the impurity limit could be further reduced to $\leq 0.3\%$ for Li and $\leq 0.1\%$ for Ca. Full details of the x-ray diffraction and scanning electron microscopy experiments will be published elsewhere [13].

At ambient pressure no superconductivity could be detected in $CaLi_2$ either in the electrical resistivity to 2 K (samples *A* and *B*) nor in sensitive ac susceptibility measurements to 1.10 K (sample *B*) where even a 0.03% shielding effect would have been detected. High-pressure experiments were carried out using two different DACs, one (type 1) designed by one of the authors (J. S. S.) [14] and the other (type 2) brought by a second author (T. M.) from Osaka University. The type-1 DAC uses two opposing 1/6-carat, type Ia diamond anvils with 0.3 or 0.5 mm diameter culets, whereas the culet diameter in the type-2 DAC, with 1/4-carat synthetic type Ib diamonds, is 0.3 mm. Re and W-25 at.% Re gaskets (thickness ~0.25 mm) are used in the resistivity and ac susceptibility studies, respectively. The superconductivity of the latter gaskets at 5 K restricts the search for superconductivity in $CaLi_2$ in the present ac susceptibility studies to temperatures above 5 K. Tiny ruby spheres [15] are placed on the sample to allow the pressure determination using the revised ruby calibration of Chijioke *et al.* [16] with resolution ±0.2 GPa.

A standard four-point ac electrical resistivity technique is used at 13 Hz frequency with a Stanford Research SR830

digital lock-in amplifier. The sample is approximately 100 μm in diameter and 10 μm thick, the voltage leads being approximately 20–30 μm apart. No pressure medium is used so that the pressure applied to the sample is best characterized as "nonhydrostatic." As a result of the pressure gradient across the sample and the sizeable shear stress on the ruby spheres, the width of the R_1 ruby fluorescence line [17] is as large as ±15 GPa (see Fig. 3 below). In the type-1 DAC the ac susceptibility is measured using two compensated primary or secondary coil systems, one around the diamond anvils and the other just outside. For signal detection the SR830 lock-in amplifier is used with an applied field of 3 Oe rms at 1023 Hz. As in the resistivity measurements, no pressure medium is used. The width of the ruby R_1 line is a good deal narrower than in the resistivity studies, as seen in Fig. 3. Further details of the DAC techniques used in the electrical resistivity [18] and ac susceptibility [13,14,19] measurements are given elsewhere.

The results of the present electrical resistivity measurements on sample *A* are shown in Fig. 1. The abrupt drop in the resistance below 15 K for pressures at or above 11 GPa is the signature of a superconducting transition. As the pressure is increased above 11 GPa, the transition is seen to shift to higher temperatures, reaching a maximum value near 13 K for $P \approx 40$ GPa. Except for the measurement at 52 GPa, the normal-state resistivity is seen to rapidly increase with pressure over the entire temperature range up to the highest pressure measured (81 GPa). That this rapid resistivity increase is quite reversible, and thus not mainly due to the addition of lattice defects as the sample is plastically deformed by the nonhydrostatic pressure, is
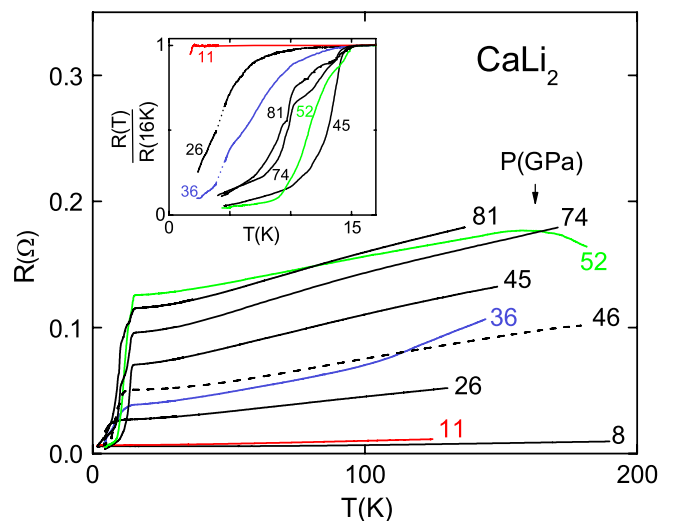

FIG. 1 (color online). Electrical resistance versus temperature for $CaLi_2$ (sample *A*) at pressures 8, 11, 26, 36, 45, 52, 74, 81, 46, taken in that order. Inset shows data plotted as resistance normalized at 16 K versus temperature to 17 K; dots bridge gap in data at 26 and 36 GPa.

seen from the final set of data at 46 GPa (dashed line in Fig. 1) where the pressure was reduced from 81 GPa. This conclusion is also supported by purely hydrostatic pressure studies to 0.76 GPa in our He-gas pressure system where the resistivity is found to increase rapidly and reversibly over the measured temperature range 14–300 K, the rate of increase at ambient temperature being $+13.3(3)\%$/GPa. This large pressure-induced increase in the normal-state resistivity with pressure is analogous to that found in elemental Li [2,5] and Ca [8] and corroborates the predictions of Feng *et al.* [11] that the electronic properties of $CaLi_2$ should become highly anomalous under pressure. Full details of the resistivity studies will be given elsewhere [13].

A much superior test for bulk superconductivity than the electrical resistivity is to search for the onset of strong diamagnetic shielding in the magnetic susceptibility. In Fig. 2 we plot the real part of the ac susceptibility versus temperature for monotonically increasing pressure. Whereas no diamagnetic transition is visible above 5 K at 25 GPa, at 35 GPa strong diamagnetic shielding consistent with 70%–100% flux expulsion is seen below 12 K. At somewhat higher pressures the superconducting transition temperature T_c passes through a maximum before falling off rapidly to temperatures below 5 K for $P \approx 54$ GPa. As expected for a superconducting transition, the diamagnetic signal for 39 GPa is seen in the inset to Fig. 2 to shift by 0.62 K to lower temperatures if a dc magnetic field of 500 Oe is applied. The same field shifts T_c down by 0.54 K at 35 GPa and by 0.48 K at 43 GPa. The small magnitude of these field-induced shifts gives evidence that $CaLi_2$ is a type II superconductor.
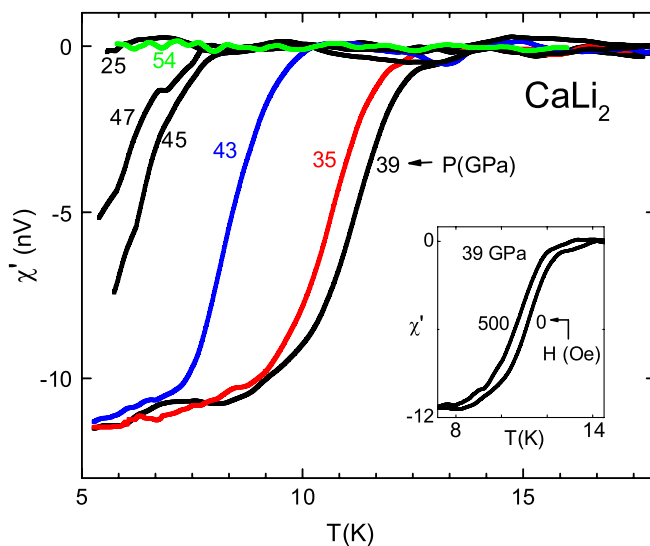
In Fig. 3 the measured values of T_c are plotted versus pressure for both the resistivity and ac susceptibility measurements. Here T_c is defined from the transition midpoint, rather than from the transition onset [20]. For applied pressures above 11 GPa, $T_c(P)$ from both sets of measurements is seen to initially shift under pressure to higher temperatures but then to pass through a maximum near 12 K for $P \approx 40$ GPa. The differences in the $T_c(P)$ dependences in resistivity and susceptibility measurements likely arise from the appreciable pressure gradients across the sample and/or shear stress effects in these nonhydrostatic experiments. The susceptibility measurement should yield the more intrinsic $T_c(P)$ dependence since it is a superior measurement of bulk superconductivity. The rather sharp peak in $T_c(P)$ near 40 GPa, particularly in the susceptibility measurement, suggests a structural phase transition at this pressure. Indeed, Feng *et al.* [11] predict for hcp $CaLi_2$ significant lattice bifurcation at pressures $\gtrsim 47$ GPa. A synchrotron radiation study at ambient temperature revealed no clear evidence of any structural phase transitions to 20 GPa [13]; an extension of these studies to higher pressures and lower temperatures would be of particular interest since they would reveal whether the pressure-induced superconductivity in $CaLi_2$ might be related to structural phase transitions.

In summary, samples of the hexagonal Laves-phase compound $CaLi_2$ have been prepared and characterized. At ambient pressure no superconductivity is found above 1.10 K. Under pressures above 11 GPa, a superconducting transition is observed in both the electrical resistivity and
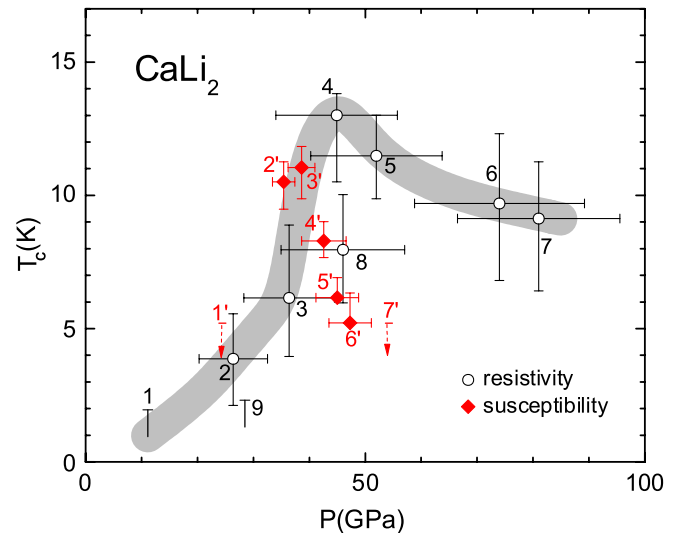
FIG. 2 (color online). Real part of ac susceptibility versus temperature for $CaLi_2$ (sample *B*) for pressures 25, 35, 39, 43, 47, 54, taken in that order. In the inset, the superconducting transition for 39 GPa pressure shifts by 0.62 K to lower temperatures in 500 Oe dc magnetic field.

FIG. 3 (color online). Superconducting transition temperature T_c of $CaLi_2$ versus pressure from resistivity ($\circ$) and ac susceptibility ($\blacklozenge$) measurements in Figs. 1 and 2. Value of T_c is determined from transition midpoint; vertical "error bars" give 20–80 transition width. Horizontal "error bars" reflect width of R_1 ruby peak. Primed and unprimed numbers give order of measurement. Broad gray line is a guide to the eye.

ac susceptibility at temperatures as high as 13 K. The electrical resistivity increases by a remarkable amount to 81 GPa, the highest pressure in this experiment. These results thus lend support to the prediction by Feng *et al.* [11] that, as for Ca and Li, the electronic properties in $CaLi_2$ become highly anomalous under pressure. High-pressure studies would also be very interesting on the nominally immiscible Li-Be system which has been predicted to form a number of stable stoichiometric compounds under high pressure which exhibit quasi-two-dimensional electronic structure [21]. Were one or more of these compounds to become superconducting, higher values of T_c than for $CaLi_2$ might be anticipated due to their low molecular weight.

*Permanent address: KYOKUGEN, Center for Quantum Science and Technology under Extreme Conditions, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan.

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[20] In a nonhydrostatic pressure cell an appreciable pressure gradient exists across the sample, the pressure reaching its maximum in the center. If the intrinsic $T_c(P)$ dependence passes through a maximum, the region of the sample responsible for the onset temperature shifts from the cell middle to the cell perimeter with increasing pressure which may cause $T_c^{onset}(P)$ to "hang up" at its maximum value. In this situation the transition midpoint more closely reproduces the intrinsic $T_c(P)$ dependence.

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