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Response of Superconductivity and Crystal Structure of LiFeAs to Hydrostatic Pressure

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Abstract: On the application of hydrostatic pressures of up to 1.3 GPa, the superconducting transition temperatures (T_c) of samples of LiFeAs are lowered approximately monotonically at approximately -2 K GPa^{-1}. Measurements of the X-ray powder diffraction pattern at hydrostatic pressures of up to 17 GPa applied by a He gas pressure medium in a diamond anvil cell reveal a bulk modulus for LiFeAs of 57.3(6) GPa which is much smaller than that of other layered arsenide and oxyarsenide superconductors. LiFeAs also exhibits much more isotropic compression than other layered iron arsenide superconductors. The higher and more isotropic compressibility is presumably a consequence of the small size of the lithium ion. At ambient pressure the FeAs$_4$ tetrahedra are the most compressed in the basal plane of those in any of the superconducting iron arsenides. On increasing the pressure the Fe$-$Fe distance contracts more rapidly than the Fe$-$As distance so that the FeAs$_4$ tetrahedra become even more distorted from the ideal tetrahedral shape. The decrease in T_c with applied pressure is therefore consistent with the observations that in the iron arsenides and related materials investigated thus far, T_c is maximized for a particular electron count when the FeAs$_4$ tetrahedra are close to regular.

Introduction

High-temperature superconductivity has recently been reported in several compounds containing FeAs anti-PbO-type (i.e., antifluorite-type) layers. LaFeAsO with the ZrSiCuAs structure type (Figure 1) was found to superconduct at up to about 26 K when doped with electrons through the substitution of about 10$-$20% of the oxide ions by fluoride.[1] T_c is increased when larger amounts of fluoride are incorporated in high-pressure syntheses.[2] Substitution of lanthanum in LaFeAsO$_{1-x}$F$_x$ by heavier and smaller lanthanides[3-5] results in higher T_cs, and it has been shown that electron doping by introduction of oxygen deficiency leads to T_cs of up to 55 K in SmFeAsO$_{1-x}$.[6] Very recently, derivatives of AFeAsF (A = Ca, Sr, Eu) isostructural with LnFeAsO (Ln = lanthanide) have also been shown to
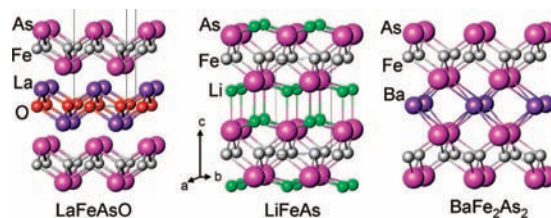

Figure 1. Crystal structure of LiFeAs (center) compared with the structures of representative members of the other families of superconducting layered arsenides.

exhibit superconductivity.[7-10] BaFe$_2$As$_2$ with the common ThCr$_2$Si$_2$ structure type (Figure 1) was found[11] to exhibit qualitatively very similar magnetic and structural behavior to LaFeAsO.[12] Reducing the electron count of BaFe$_2$As$_2$ to form Ba$_{1-x}$K$_x$Fe$_2$As$_2$ produced superconductivity below 38 K,[13] and

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similar doping of $SrFe_2As_2$ also produced superconductivity below 38 K.[14,15] The high T_cs and critical fields exhibited by these superconductors and their proximity to magnetically ordered phases[12] suggest that they are unconventional superconductors with properties which cannot be described within the framework of existing models of superconductivity such as the BCS theory. Unlike the well-known layered cuprate superconductors, which are derived from insulating antiferromagnetic Cu^{2+} phases by hole or electron doping into the metallic regime, the formally Fe^{2+} compounds such as LaFeAsO and $BaFe_2As_2$ are metallic, and formal electron or hole doping is not always required to drive the materials into the superconducting regime.

Some of us,[16] in parallel with other groups,[17,18] recently described superconductivity at temperatures below 18 K in LiFeAs (formally Fe^{2+}) (Figure 1), and we recently demonstrated that superconductivity occurs below at least 9 K in a new compound NaFeAs which is isostructural with LiFeAs.[19] Superconductivity with unusually high T_c is not confined to iron-containing arsenides: α-FeSe, with a structure composed of anti-PbO-type FeSe layers with no interlayer species, was found to exhibit superconductivity at about 8 K[20] and showed a dramatic enhancement of T_c up to 27 K under an applied pressure of 1.48 GPa.[21] In the superconductors based on LaFeAsO the aliovalent substitution of O by F and the isovalent substitution of La^{3+} by heavier and smaller lanthanides reduces the lattice parameters and corresponds to exerting a "chemical pressure" on the system which changes the structure of the FeAs layers and hence the band structure. The structural details, along with the electron count, seem to be important in determining T_c. Several authors have noted that the highest T_cs occur for compounds with $FeAs_4$ tetrahedra which are close to regular.[22,23] It has been suggested that the differences between LaFeAsO and LaFePO might be ascribed to the very different bond angles in the $FePn_4$ tetrahedra.[24]

Furthermore, it has been shown that, like in the cuprates, applied pressure is an important thermodynamic variable for controlling the properties in these iron arsenide systems. Unlike in conventional BCS superconductors in which T_c is lowered on application of pressure, it has been shown that application of pressure produces a significant enhancement in T_c in some layered arsenides. In the original 26 K superconductor $LaFeAsO_{0.89}F_{0.11}$ a T_c of 43 K was achieved under an applied hydrostatic pressure of 5 GPa.[25] Furthermore, nonsuperconducting $LaFeAsO^{26}$ may be driven into the superconducting regime by application of pressure with a T_c of 21 K attained at 12 GPa.[26] Pressure-induced superconductivity was reported in the high-pressure "collapsed tetragonal" phase of $CaFe_2As_2$,[27,28] However, more recent work showed that this was an artifact of nonhydrostatic compression.[29] Under hydrostatic pressure stoichiometric $CaFe_2As_2$ does not exhibit superconductivity, and the origin of the superconductivity observed reproducibly under nonhydrostatic conditions is not yet clear. Pressure-induced superconductivity has also been reported in $SrFe_2As_2$ and $BaFe_2As_2$,[30,31] although the onset of superconductivity has not yet been correlated with any changes in crystal structure. The structural changes in $CaFe_2As_2$ occur at modest pressures and have been well described.[32,33] The behavior of these iron arsenides under applied pressure underlines the complex nature of these materials. The precise behavior seems to be very sensitive to composition. For example, a sample $LaFeAsO_{0.89}F_{0.11}$ shows an enhancement of T_c up to 5 GPa, and application of higher pressures leads to a decrease of T_c, the ambient pressure value being equalled at 16 GPa.[25] A less fluoride-rich sample, $LaFeAsO_{0.95}F_{0.05}$, shows a less significant increase in T_c on the initial application of pressure.[25] Other authors found qualitatively similar behavior (i.e., T_c increases initially with pressure and is then suppressed) for another $LaFeAsO_{0.89}F_{0.11}$ sample as well as for high-pressure-synthesized phases of nominal compositions $LaFeAsO_{0.7}$ and $LaFeAsO_{0.5}F_{0.5}$.[34] A material of reported composition $NdFeAsO_{0.6}$ shows an almost linear decrease of T_c from the ambient pressure value of about 54 K to about 16 K under an applied pressure of 18 GPa,[35] and $LnFeAsO_{0.85}$ (Ln = Nd, Sm) show

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similar behavior.[36] In the series of compounds $SmFeAsO_{1-x}F_x$ ($0 \leq x \leq 0.2$), enhancement of T_c under applied pressures of up to 1.2 GPa is observed for $x \leq 0.12$, while for $x \geq 0.15$ T_c is lowered from the ambient pressure values.[37,38] For the $Sr_{1-x}K_xFe_2As_2$ system the behavior of T_c as a function of pressure is also dependent on the electron count.[39] It has been suggested that the observed pressure dependence of T_c in $LaFeAsO_{1-x}F_x$ phases is a consequence of both changing the orbital degeneracy and the density of states at the Fermi level[34,40] and that the pressure dependence of T_c in the iron arsenides may be quite different from that in the layered cuprate superconductors.[26] However, many further experimental and computational studies on these systems are required before an accurate overall picture of the correlations between properties, composition, structure, and electron count will emerge.

Here we describe the behavior of LiFeAs under pressure using a combination of magnetometry and synchrotron X-ray powder diffraction measurements. The behavior of this compound is compared with the available data on other iron arsenides and chalcogenides.

Experimental Section

Synthesis. All manipulations of solids were carried out in a Glove Box Technology dry box containing recirculated argon with a combined O_2 and H_2O content of less than 5 ppm. Powder samples of LiFeAs were prepared by the methods described in refs 16 and 17, and the presence of superconductivity was confirmed by DC SQUID magnetometry. Two samples were selected for the magnetometry investigations under pressure, and these were the same samples as some of us have investigated using muon-spin rotation (μSR) measurements.[41] Sample 1 with $T_c = 16$ K and lattice parameters $a = 3.774(1)$ Å, $c = 6.353(1)$ Å, and $V = 90.5(1)$ Å^3 was prepared by heating a 1:1:1 ratio of the elements in a sealed tantalum tube at 750 °C for 24 h, a method similar to that described by Tapp et al.[17] Sample 2 with $T_c \approx 12$ K and a broader superconducting transition than that observed for other reported samples was the same as that was labeled sample 2 in ref 16 ($a = 3.774(1)$ Å, $c = 6.354(2)$, $V = 90.5(1)$ Å^3). Powder X-ray diffraction indicated that sample 1 contained 0.7 mol % Li_7TaAs_4 and sample 2 contained 1.5 mol % FeAs as impurities. We presume that the differences in T_c result from compositional differences smaller than can be resolved using diffraction methods. μSR measurements[16] showed that both samples contained a large superconducting fraction (>80%).

High-Pressure X-ray Powder Diffraction. Measurements were carried out on sample 2 on the beamline ID27 at the ESRF, Grenoble, France. The sample was loaded in two different membrane-driven diamond-anvil cells (DAC) equipped with 350 (for run 1, which failed at 15 GPa) or 600 μm (for run 2, up to 17 GPa followed by decompression) culet diamonds. In both cases, all cell manipulation was carried out in the Ar atmosphere glovebox of the ESRF Chemistry Laboratory. Once the sample was included in the stainless steel gasket, along with a ruby for pressure

measurement,[42] it was sealed and transferred to the high-pressure gas-loading facility. The DAC was opened under high He pressure, flushed, and gas loaded with an initial gas pressure of less than 1 kbar. Diffraction patterns were measured for about 1 min each at up to 17.1 GPa using 0.3738 Å X-rays, focused to 5 μm × 7 μm, and collected on a Mar345 image plate reader. Detector calibration, correction of distortion, and integration to conventional 2θ-intensity data were carried out with Fit2D.[43] Measurements were made both during compression (runs 1 and 2) and decompression (run 2) of the sample. Model-independent LeBail-type analyses and Rietveld analyses were performed using the GSAS suite[44] and the EXPGUI interface.[45]

Magnetometry. AC susceptibility measurements were carried out using a Quantum Design MPMS XL-7 SQUID magnetometer in the temperature range 2−30 K using a 4 Oe AC field and a 10 Hz driving frequency. Approximately 6 mg of each LiFeAs sample was intimately mixed with the pressure transmitting medium Apiezon J oil in the glovebox and then loaded into a 7.5 mm long cylindrical Teflon cell. The cylindrical sample space was 1.7 mm in diameter and 3.5 mm long. Care was taken to avoid including argon gas from the glovebox atmosphere, and a small piece of elemental tin was included for pressure calibration purposes.[46] The Teflon cell was inserted into a piston cylinder pressure cell (HMD Corp., CC-Spr-8.5-MC4), designed to be installed into the magnetometer, which allowed pressures of more than 1.3 GPa to be achieved at liquid helium temperatures. Measurements of the susceptibility were made on warming after cooling in zero field.

Results and Discussion

Magnetic Properties. Sample 1 shows a sharp superconducting transition at about 16 K at ambient pressure as has been observed previously for LiFeAs,[16−18] while sample 2 shows a much broader superconducting transition and T_c is apparently lower (12 K). DC susceptibility measurements[16] suggest that the superconducting volume fraction is significantly lower in sample 2 than in sample 1 based on the size of the zero-field-cooled diamagnetic susceptibility. However, this may be an artifact of differing particle sizes as the μSR results suggested that both samples reported here were composed of at least 80% superconducting material.[41] The cell volumes of the two samples are equal within experimental uncertainty, and comparison of sample 2 with another sample magnetically similar to sample 1 showed no compositional or structural differences within the uncertainty of the neutron powder diffraction experiments;[16] the differences in T_c may be a consequence of very small compositional differences. In the current measurements of the magnetic susceptibility as a function of pressure, T_c was estimated from the real part of the AC susceptibility (Figure 2) as the temperature at which a line coincident with the steeply rising portion of the susceptibility intersects with a line coincident with the normal state susceptibility just above the superconducting transition as shown in Figure 2. Measurements at up to 1.3 GPa revealed an approximately linear decrease of T_c with increasing pressure for both samples as shown in Figure 3. Sample 1, with the higher ambient pressure T_c, shows a decrease in T_c with applied pressure of $-1.7(2)$ K GPa^{-1}, while the corresponding value for sample 2 is similar within the experimental uncertainty at $-2.0(2)$ K GPa^{-1}.

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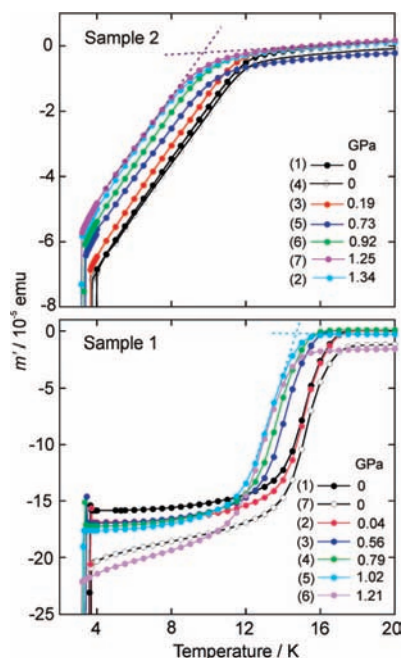
Figure 2. Real part of the AC susceptibility as a function of pressure for samples 1 and 2. The sharp drop in susceptibility between 3 and 4 K arises from the elemental tin used to measure the pressure. For two of the curves the dotted lines show how T_c was estimated from their intersection. The numbers in parentheses indicate the order in which the measurements were performed for each sample.
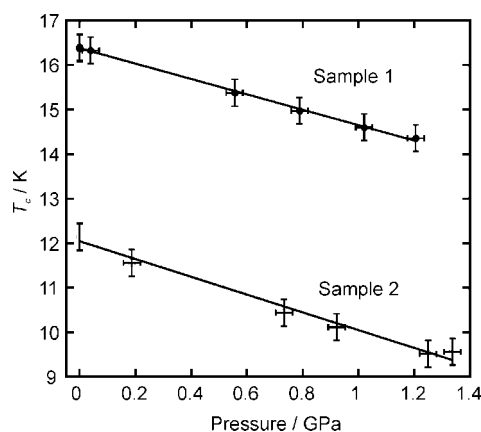

Figure 3. Variation of T_c with applied hydrostatic pressure. The lines are linear fits to the data (see text).

Crystal Structure. Rietveld and model-independent LeBail-type fits to the data were carried out with the peak profile described by an angle-independent Gaussian component and a Lorentzian component to describe strain broadening. LeBail fits were used to describe the behavior of the lattice parameters as functions of pressure. In the Rietveld refinements the only atomic coordinate which was refined was the *z* coordinate of As; due to the almost negligible contribution made by Li to the Bragg intensities the position of this atom was not refined. A single isotropic displacement parameter was refined, and a single March–Dollase term was employed to account for preferred orientation effects. Comparison of the results obtained using this March–Dollase treatment and an alternative spherical harmonic treatment of the preferred orientation in the Rietveld analysis revealed consistent structural models within the uncertainty in the refined parameters, although the correlation between the As coordinate and the preferred orientation
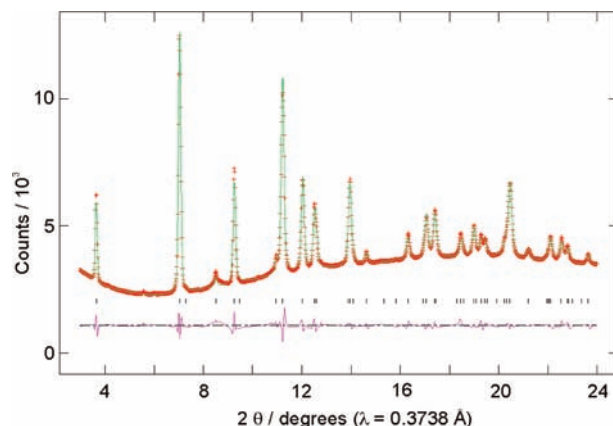

Figure 4. Results of Rietveld refinement against data collected at 17 GPa. The data (red points), fit (green line), and difference (lower purple line) are shown together with tick marks indicating the reflection positions.

parameters was just greater than the threshold for report by GSAS (0.5). The Rietveld refinement against the data obtained at 17 GPa is shown in Figure 4. Given that there are significant parameter correlations and the fact that it is widely recognized that the estimated standard deviations on the refined parameters obtained from GSAS are usually underestimates, the error bars in Figures 5 and 6 have been set equal to five times the estimated standard deviations obtained in GSAS.[47]

Inspection of the lattice parameters, determined by LeBail refinement of upstroke data (i.e., data collected on compression) from the two runs, shows that the lattice parameters vary smoothly over the full range to 17 GPa. The behavior of the lattice parameters, *a* and *c*, the cell volume, *V*, and the *c/a* ratio with pressure are shown in Figure 5. From finite strain analysis we estimated a bulk modulus of 56.7 GPa and identified a positive-sloping strain-normalized pressure behavior, indicating that a fit to a third-order Birch–Murnaghan equation of state (EoS)[48]

$$P = \frac{3K_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left\{1 - \frac{3}{4}(4 - K'_0)\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]\right\}$$

was required to express the behavior of the cell volume, *V*, with pressure, *P*, using 42 data sets obtained on upstroke. Using the EosFit5.2 software[49] we obtained the following parameters: V_0 = 90.356(4) Å^3 with an ambient pressure bulk modulus K_0 of 57.3(6) GPa and a value of K'_0 = 4.5(1) for the first pressure derivative of K_0. Similar treatment of the cell parameter data using a parametrized third-order equation, where cell volume is replaced by a^3 or c^3, results in two distinct axial compressibilities. The *a* axis is the less compressible and stiffens more sharply with pressure (K_a = 65.6(8) GPa, K_a' = 4.9(15)) than the *c* axis (K_c = 45.3(6) GPa, K_c' = 3.9(1)). This behavior is consistent with the higher atom densities in the basal plane compared with the atom density along the stacking direction of the layers, *c*. This difference in overall compressibility along the two axial directions leads to a fairly smooth decrease in *c/a* by 2% at 17 GPa (Figure 5).

For comparison, the compressibility of LiFeAs is intermediate between those of two FeS polymorphs: MnP-type FeS has a bulk modulus of 35(4) GPa, and troilite FeS has a bulk modulus

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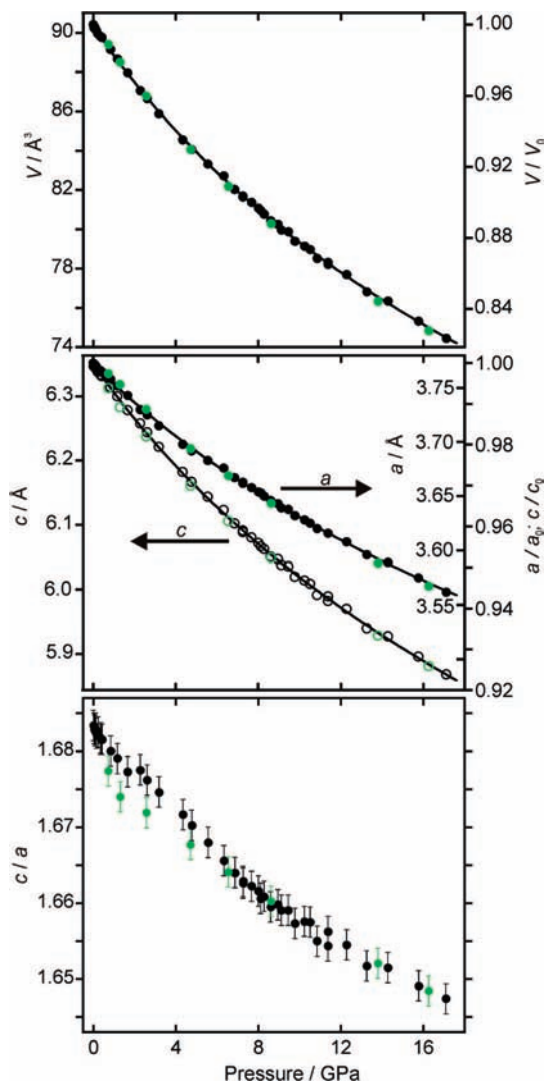(49) Angel, R. J. *Rev. Min. Geochem.* **2000**, *41*, 35.

Figure 5. Variation with pressure of lattice parameters and cell volume obtained from LeBail-type fits to the diffraction data obtained from upstroke (pressure increasing) runs (black symbols) and on downstroke (pressure decreasing) runs (green symbols). Error bars equal to 5 times the esd derived from GSAS lie within the points used for the cell parameters and volume. The solid lines are fits to the upstroke data only using a third-order Birch–Murnaghan EoS (for further details see text). a_0, b_0, and V_0 are the values of the parameters at ambient pressure.
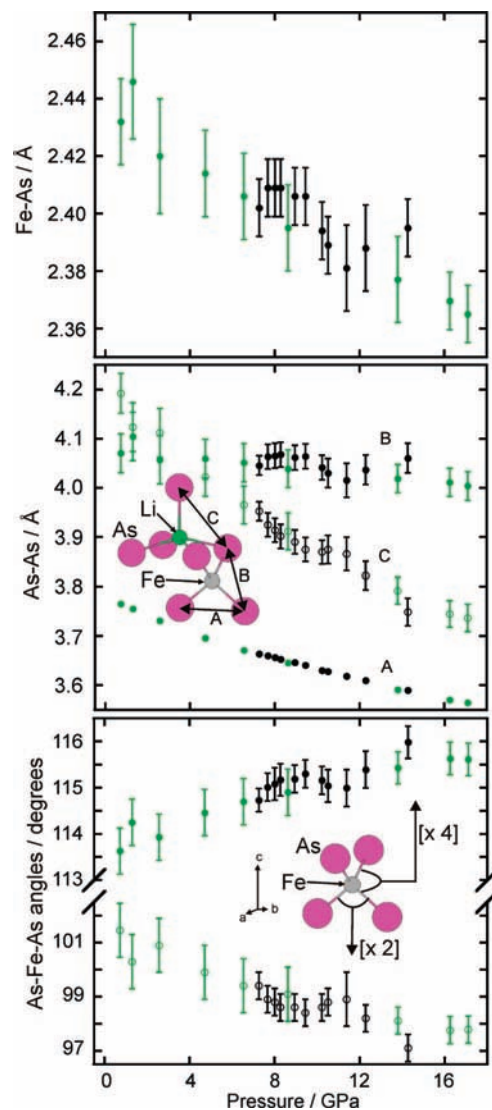

Figure 6. Variation of interatomic distances and bond angles with pressure. The error bars are equal to 5 times the esds on the values produced by GSAS. Black symbols denote measurements made during compression (upstroke); green symbols denote measurements made during decompression (downstroke). Note that the As–As distance designated A is equal to the lattice parameter a and carries a smaller esd than the other As–As distances.

of 82(7) GPa.[50] It is most instructive to compare the bulk modulus of LiFeAs and the anisotropy in the compressibility with those of other superconducting iron arsenide compounds. LiFeAs has a similar bulk modulus to that of $CaFe_2As_2$: using the data in ref 32 in which high-pressure neutron diffraction studies were carried out on $CaFe_2As_2$ up to 0.6 GPa, one can estimate a bulk modulus for $CaFe_2As_2$ of about 60 GPa at 50 K. However, $CaFe_2As_2$ has a different structure and behaves very differently to LiFeAs, undergoing a phase transition to a less compressible so-called "collapsed tetragonal" phase at 0.3 GPa. $CaFe_2As_2$ is much more compressible in the c direction than in the basal plane, and the anisotropy in the compressibility is much greater than that of LiFeAs. This is consistent with the observation that the phase transition in $CaFe_2As_2$ at 0.3 GPa, which occurs with a sharp drop in volume, occurs with a

dramatic contraction of c but an expansion of the basal lattice parameter a. Among the oxyarsenides $LaFeAsO_{0.9}F_{0.1}$[51] has a bulk modulus of 78(2) GPa, while $NdFeAsO_{0.88}F_{0.12}$[52] with a 2% smaller ambient-pressure cell volume than the La analogue is correspondingly stiffer with a bulk modulus of 102(2) GPa. $LaFeAsO_{0.9}F_{0.1}$ shows no phase transition up to 32 GPa, but $NdFeAsO_{0.88}F_{0.12}$ is reported to undergo a phase transition above about 12 GPa to a less compressible phase which apparently has the same symmetry as the low-pressure phase.[52] In $NdFeAsO_{0.88}F_{0.12}$, like in $CaFe_2As_2$, the phase transition is accompanied by an increase in the basal lattice parameter a and a contraction in the lattice parameter c, but in this case, unlike in $CaFe_2As_2$,[32,33] there is no dramatic change in the cell volume.

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The oxyarsenides are much less compressible in the basal plane than LiFeAs, presumably because of the rigidity of the fluorite-type oxide layers. At 10 GPa the basal lattice parameter a in LiFeAs has contracted by 3.9% compared with the ambient-pressure value, whereas the comparable contractions in $LaFeAsO_{0.9}F_{0.1}$ (2.2%) and $NdFeAsO_{0.88}F_{0.12}$ (1.3%) are much smaller. In contrast, the c lattice parameter contracts by about 5.5% up to 10 GPa in LiFeAs and $NdFeAsO_{0.88}F_{0.12}$ and by 4.4% in $LaFeAsO_{0.9}F_{0.1}$. The anisotropies in the compression of both $CaFe_2As_2$ and the oxyarsenides are fairly similar and much greater than that of LiFeAs.

Despite the large uncertainty in the location of As and hence in the interatomic distances and bond angles, clear trends in the structural parameters of LiFeAs are evident (Figure 6) from the results of Rietveld refinement. The Fe–Fe distance is determined with high precision because it is proportional to the basal lattice parameter (Fe–Fe = $a/\sqrt{2}$). Our structural analysis shows that the contraction of the Fe–Fe distance with increasing pressure (5.6% up to 17 GPa) is greater than the contraction of the Fe–As distance (2.8%). Accordingly, the 4-fold As–Fe–As angle bisected by the basal plane increases with applied pressure and the 2-fold As–Fe–As angle bisected by the c axis decreases with applied pressure. As we describe elsewhere,[16] the Fe–Fe distance in LiFeAs is the shortest of any of the superconducting iron pnictides and the $FeAs_4$ tetrahedron in LiFeAs is highly distorted by compression in the basal plane. The effect of applied pressure is to further increase this distortion as indicated in Figure 6. This behavior is in contrast to the behavior in $CaFe_2As_2$[32,33] and $NdFeAsO_{0.88}F_{0.12}$.[52] In $CaFe_2As_2$ the transition to the collapsed tetragonal phase is accompanied by a dramatic distortion of the almost regular ambient-pressure $FeAs_4$ tetrahedron by compression along the c axis direction (i.e., opposite to the distortion in LiFeAs). In $NdFeAsO_{0.88}F_{0.12}$, which at ambient pressure has very similar As–Fe–As angles to those in $CaFe_2As_2$, a similar but gradual compression of the $FeAs_4$ tetrahedra along the c axis direction is evident up to about 14 GPa. The data reported in ref 52 show that the As–Fe–As angles in $LaFeAsO_{0.9}F_{0.1}$ are fairly invariant up to about 20 GPa (the 2-fold angle bisected by the c axis is about 111.5(5)°), but at higher pressures the $FeAs_4$ tetrahedra become more compressed along the c direction (the 2-fold angle becomes 115° at 32 GPa).

In LiFeAs the As anions are arranged in an approximately cubic-close-packed fashion with Fe occupying one-half of the tetrahedral sites and Li displaced somewhat from the center of each octahedral site, resulting in 5 coordination of Li by As in a square pyramid. The behavior of the As–As distances with increasing pressure is revealing. The As–As distance within the basal plane which corresponds to two edges of the $FeAs_4$ tetrahedra and the basal edges of the $LiAs_5$ square-based pyramids decreases by 5.6% up to 17 GPa (this distance is equal to the lattice parameter a and is labeled A in Figure 6). The remaining four edges of $FeAs_4$ tetrahedra remain fairly constant as the tetrahedra distort (B in Figure 6), while the four apical edges of the $LiAs_5$ square-based pyramids (C in Figure 6) decrease the most rapidly: by almost 11% up to 17 GPa. Our X-ray diffraction data do not allow us to locate the Li ion accurately, but from the analysis of the changes in As–As distances it seems inevitable that the mean Li–As distance contracts more rapidly with increasing pressure than the Fe–As distance. The contrasting structural behavior of LiFeAs with pressure compared with that of representative members of the other classes of superconducting iron arsenides is likely due to

the small radius of the Li ion resulting in a high compressibility of the $LiAs_5$ polyhedron. Further measurements on LiFeAs will include investigation of the changes in the Li positions at high pressure using neutron diffraction.

As to the decrease of T_c with increasing pressure in LiFeAs, there appears to be a strong correlation between the shape of the $FeAs_4$ tetrahedra and T_c as a result of the sensitivity of the density of states at the Fermi level to the As–Fe–As angles.[23,53] In the LnFeAsO-derived superconductors the maximum T_c occurs when the $FeAs_4$ tetrahedra are close to regular providing the electron count is optimized.[22,23] Evidently superconductivity can still be supported in systems with highly distorted $FeAs_4$ tetrahedra: LiFeAs has $FeAs_4$ tetrahedra which are highly compressed in the basal plane (the two tetrahedral angles differ by 10°),[16,17] and the relatively small value of T_c lends support to the notion that regular $FeAs_4$ tetrahedra are optimal. In light of these observations it is not surprising that superconductivity is suppressed in LiFeAs on application of pressure as the $FeAs_4$ tetrahedra distort even further away from regular. In $NdFeAsO_{0.88}F_{0.12}$ the tetrahedra distort away from regular below 10 GPa[52] but in the opposite sense to those in LiFeAs; preliminary measurements on $NdFeAsO_{0.85}$ in the hydrostatic regime find a similar pressure dependence of the tetrahedral shape.[54] While the dependence of T_c on pressure for the sample of $NdFeAsO_{0.88}F_{0.12}$ reported in ref 52 has not been established, it has been found for $CeFeAsO_{0.88}F_{0.12}$[55] and $NdFeAsO_{0.85}$[36] that T_c has its maximum at ambient pressure and diminishes at high pressure, presumably as the tetrahedra distort away from regular by squashing along the c-axis direction. In the case of $LaFeAsO_{1-x}F_x$ samples the precise relationship between T_c and pressure seems to be sensitive to electron count,[25,51] but if $LaFeAsO_{0.9}F_{0.1}$ is representative of the structures of these phases with the largest lanthanide ion then the observation[51] that the $FeAs_4$ tetrahedra retain their shape up to about 20 GPa is not inconsistent with the failure to suppress T_c with applied pressures in some samples.[25,34] The squashing of the $FeAs_4$ tetrahedra along the c direction which occurs in $LaFeAsO_{0.9}F_{0.1}$ above 20 GPa[51] is consistent with the decrease in T_c observed in all $LaFeAsO_{1-x}F_x$ which have been measured up to and beyond this pressure.[25,34,51]

If the linear decrease of T_c with pressure continues to higher pressures in LiFeAs one would expect superconductivity to be completely suppressed above about 6 GPa. We note that α-$FeSe_{0.92}$ has $FeSe_4$ tetrahedra which are almost as compressed in the basal plane as those in LiFeAs (Se–Fe–Se angles of 104.34(3)° ($\times 2$) and 112.10(1) ($\times 4$)) at ambient temperature and pressure[56] and is a superconductor, while superconductivity in the analogous $FeTe_{0.92}$ is suppressed and in this case the tetrahedra are even more compressed in the basal plane than in LiFeAs at 17 GPa (Te–Fe–Te angles of 95° ($\times 2$) and 117 ($\times 4$)).[57] These observations are in line with the general observation, shown pictorially in Figure 7 of ref 23, that high-temperature superconductivity seems to be favored in systems

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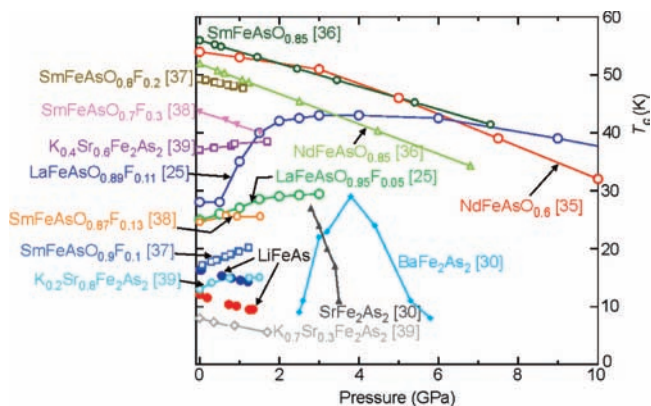
Figure 7. Comparison of the variation of T_c with applied pressure for several iron arsenide superconductors. References indicated in square brackets.

with fairly regular tetrahedra providing the electron count is optimized also. The T_c for LiFeAs is equal to the value which would be predicted by the graph of 2-fold As—Fe—As angle against T_c shown in Figure 7 of ref 23. Figure 7 of this current work summarizes the effect of pressure on superconducting transition temperatures for many layered iron arsenide systems; in very few cases have detailed analyses of the crystal structures been carried out, so it is premature to speculate about the precise origin of all these dependencies.

Conclusions

We have shown that the superconductivity in two different samples with compositions close to LiFeAs and very similar lattice constants is suppressed on application of pressure up to at least 1.3 GPa (13 kbar). Investigation of the changes in crystal structure of one of the samples up to 17 GPa reveals no structural transitions but smooth variation in the structural parameters. At ambient pressure LiFeAs has the shortest basal lattice

parameter, and hence Fe—Fe distance, of any of the layered iron arsenide superconductors. The most striking feature of the evolution of the structure of LiFeAs at high pressure is the high compressibility resulting from the ease of contraction of the $LiAs_5$ coordination polyhedron. This results in a higher compressibility in the basal plane than is observed in other layered iron arsenide superconductors. The consequence of this high basal-plane compressibility is that the unusual structural features of LiFeAs (short Fe—Fe distances and $FeAs_4$ tetrahedra that are highly compressed in the basal plane) are further enhanced on application of hydrostatic pressure. The decrease in T_c accompanying the increasing departure of the $FeAs_4$ tetrahedra from regular is in line with the observation that a high T_c in these compounds is generally favored by regular $FeAs_4$ tetrahedra. LiFeAs should be a valuable compound for computational studies which, together with further experimental studies on this and other related compounds, will shed light on the relationship between superconducting T_c, electron count, and the details of the structure of the FeAs layers.

Note Added in Proof. As this article was going to press we became aware of AC susceptibility measurements on LiFeAs at pressures of up to 1.8 GPa by Gooch et al. which are consistent with those reported here. Gooch, M.; Lv, B.; Tapp, J.H.; Tang, Z.; Lorenz, B.; Guloy, A.M.; Chu, P.C.W. *Europhys. Lett.* **2009**, *85*, 27005.

Supporting Information Available: List of refined structural parameters used to produce Figures 5 and 6 along with representative X-ray diffractograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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