FAST TRACK COMMUNICATION

Synthesis and properties of CaFe$_2$As$_2$ single crystals

F Ronning$^1$, T Klimczuk$^{1,2}$, E D Bauer$^1$, H Volz$^1$ and J D Thompson$^1$

$^1$ Los Alamos National Laboratory, Los Alamos, NM 87545, USA
$^2$ Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza 11/12, 80-952 Gdansk, Poland

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Abstract

We report the synthesis and basic physical properties of single crystals of CaFe$_2$As$_2$, a compound isostructural to BaFe$_2$As$_2$ which has been recently doped to produce superconductivity. CaFe$_2$As$_2$ crystallizes in the ThCr$_2$Si$_2$ structure with lattice parameters $a = 3.887(4)$ Å and $c = 11.758(23)$ Å. Magnetic susceptibility, resistivity, and heat capacity all show a first order phase transition at $T_0 = 171$ K. The magnetic susceptibility is nearly isotropic from 2 to 350 K. The heat capacity data gives a Sommerfeld coefficient of $8.2 \pm 0.3$ mJ mol$^{-1}$ K$^{-2}$, and does not reveal any evidence for the presence of high frequency (>300 K) optical phonon modes. The Hall coefficient is negative below the transition, indicating dominant n-type carriers.

(Some figures in this article are in colour only in the electronic version)
Figure 1. Crystal structure of CaFe$_2$As$_2$.

Figure 2. Powder x-ray diffraction pattern (Cu Kα radiation) for CaFe$_2$As$_2$. Vertical bars at the bottom represent the Bragg peak positions for the ThCr$_2$Si$_2$ tetragonal (I4/mmm) structure with refined cell parameters $a = 3.887(4)$ Å and $c = 11.758(23)$ Å. Miller indices for each peak are shown, and a peak from the Sn flux is marked with an arrow.

Figure 3. Magnetic susceptibility $\chi(T)$ of CaFe$_2$As$_2$ measured in a magnetic field $H = 5$ T for $H \parallel ab$ (black-circles) and $H \parallel c$ (blue triangles). A structural transition is indicated by the sharp drop at $T_0 = 172$ K (dashed line) in $\chi_c$ and $\chi_{ab}$.

Figure 4. Specific heat versus temperature is shown for CaFe$_2$As$_2$. The dashed line represents a simple lattice estimate as described in the text. The top inset displays the relaxation curve at the transition temperature. The lower inset displays the low temperature heat capacity. The solid line is a fit to $C/T = \gamma + \beta T^2 + \alpha T^4$.

The magnetic measurements were performed from 1.8 to 300 K using a commercial SQUID magnetometer. Specific heat measurements were carried out using an adiabatic method in a commercial cryostat from 2 to 300 K. Electrical transport measurements were performed using a LR-700 resistance bridge with an excitation current of 1 mA, on samples for which platinum leads were spot welded.

The magnetic susceptibility $\chi(T)$ of CaFe$_2$As$_2$ measured in a magnetic field $H = 5$ T with $H \parallel ab$ and $H \parallel c$ is shown in figure 3. The susceptibility is essentially isotropic over the entire measured temperature range. Close to $T_0 = 172$ K a sharp drop is evident in $\chi_{ab}$ and in $\chi_{c}$, albeit slightly smaller, likely indicating a structural transition that is similar to those observed in BaFe$_2$As$_2$ [12, 14, 18] and LaFeAsO [1].

The heat capacity presented in figure 4 reveals a very sharp symmetric anomaly consistent with a first order phase transition at 172 K (upon warming). In the top inset, the relaxation curve of sample temperature versus time is shown. While a constant heat is applied to the sample it steadily increases in temperature as dictated by the sample heat capacity and the thermal link to the bath. The plateau in the curve indicates an abrupt increase in the heat capacity as well as the latent heat associated with the first order transition [23], sharply defined in temperature at 171.8±0.1 K. The low temperature heat capacity is presented in the lower inset. Below 10 K the heat capacity data can be fit to $C = \gamma T + \beta T^3 + \alpha T^5$. This gives an electronic specific heat...
CaFe$_2$As$_2$ as a function of temperature. The inset illustrates the superconductor MgB$_2$ [24], where analysis of the heat capacity at 300 K. This is in contrast to the case of phonon-mediated few high frequency optical phonon modes with energies above of states, the fact that this gives a reasonable account of the isotopic behavior at the transition observed in resistivity for current along the $c$-axis. Thermal hysteresis at the transition observed in resistivity for current along the $c$-axis. The thermal hysteresis at the transition observed in resistivity for current along the $c$-axis. The inset illustrates the thermal hysteresis at the transition observed in resistivity for current along the $c$-axis. This is consistent with the smaller unit cell volume. However, the structural/SDW phase transition is not monotonic with cell volume even within the group IIA of the periodic table ranging from 80 to 140 K for BaFe$_2$As$_2$, and 195–205 K in SrFe$_2$As$_2$ compared with 170 K in CaFe$_2$As$_2$. (EuFe$_2$As$_2$ orders at 195 K, and the Eu moments order at 20 K [21].) The reason for this is not understood, but possibly indicates the sensitivity of the transition to details of the electronic structure. Similarly, the anisotropy of the susceptibility of CaFe$_2$As$_2$ measured at 5 T is nearly isotropic over the entire temperature range measured, both above and below the transition. Although the overall magnitude is similar to that observed in SrFe$_2$As$_2$ [16] the anisotropy is qualitatively different. In our case the low temperature Curie–Weiss tail is isotropic, and thus could originate from an impurity contribution. The isotropic behavior above the transition is more consistent with that observed in BaFe$_2$As$_2$ [14]. The role of trace amounts of ferromagnetic impurity phases such as Fe$_2$As [25], will be studied in more detail to determine the intrinsic behavior of the susceptibility. Finally, whether the current samples are affected by Sn substitution as suggested for single crystals of BaFe$_2$As$_2$ grown by a similar technique [14] must still be investigated.

We have synthesized single crystals of CaFe$_2$As$_2$, which possesses a first order transition at 170 K, which is likely a combined structural and magnetic transition. Given that superconductivity has been found by doping the isostructural Ba and Sr compounds [13, 18, 19] we believe that the Ca compound is also a likely candidate for the presence of superconductivity upon chemical substitution.

At the completion of this work we became aware of two other papers reporting the synthesis of CaFe$_2$As$_2$. Single crystals of CaFe$_2$As$_2$ grown using self-flux [26] and Sn flux [27] methods gave results similar to ours, and indeed superconductivity was found upon Na doping [26].

\[
\gamma = 8.2 \pm 0.3 \text{ mJ mol}^{-1} \text{K}^{-2}
\]

Assuming that the $T^3$ term is entirely due to acoustic phonons, from the $\beta$ coefficient = 0.383 ± 0.018 mJ mol$^{-1}$ K$^{-4}$ we extract a Debye temperature $\Theta_D = 292$ K. The dashed curve in the figure gives the lattice contribution to the specific heat based upon a simple Debye model using $\Theta_D = 292$ K. While this is certainly an oversimplification of the exact phonon density of states, the fact that this gives a reasonable account of the data at high temperatures indicates that there are relatively few high frequency optical phonon modes with energies above 300 K. This is in contrast to the case of phonon-mediated superconductor MgB$_2$ [24], where analysis of the heat capacity indicates the presence of phonon modes up to 750 K.

As with susceptibility and heat capacity, the resistivity data presented in figure 5 contains a clear first order phase transition at 170 K. The jump indicates either an increase in scattering or a decrease in the number of carriers below the transition relative to above it. The samples have a RRR ($=\rho(300 \text{ K})/\rho(4 \text{ K})$) of 10. A small partial superconducting transition at 3.8 K is due to small Sn inclusions. Data for current parallel to the $c$-axis on 4 samples (not shown) have a qualitatively similar temperature dependence, but range in absolute magnitude from 50 to 1000 times larger than the in-plane data, possibly a consequence of weakly coupled micaceous layers leading to large variations in the magnitude of the $c$-axis resistivity. The inset demonstrates the thermal hysteresis expected for a first order phase transition. Also shown in figure 5 is the Hall coefficient. The dominant carrier below the 171 K transition is electron-like. There is a rollover at 15 K which may be due to either the multiband nature of these systems, or due to localization effects. With a resolution of $2 \times 10^{-11} \Omega \text{cm Oe}^{-1}$ we cannot say whether the dominant carrier type at room temperature is also electron-like.

Briefly, we compare our results with currently available data on other members of the AFe$_2$As$_2$ compounds with A = Ba, Sr, and Eu, listed in Table 1. We note that the lattice constants monotonically decrease from BaFe$_2$As$_2$ to SrFe$_2$As$_2$ to EuFe$_2$As$_2$ to CaFe$_2$As$_2$, as one would expect given the smaller ionic radii of Ca$^{2+}$ versus Eu$^{2+}$ and Sr$^{2+}$ versus Ba$^{2+}$. The higher Debye temperature for CaFe$_2$As$_2$ (292 K) is consistent with the smaller unit cell volume. However, the structural/SDW phase transition is not monotonic with cell volume even within the group IIA of the periodic table ranging from 80 to 140 K for BaFe$_2$As$_2$, and 195–205 K in SrFe$_2$As$_2$ compared with 170 K in CaFe$_2$As$_2$. (EuFe$_2$As$_2$ orders at 195 K, and the Eu moments order at 20 K [21].) The reason for this is not understood, but possibly indicates the sensitivity of the transition to details of the electronic structure. Similarly, the anisotropy of the susceptibility of CaFe$_2$As$_2$ measured at 5 T is nearly isotropic over the entire temperature range measured, both above and below the transition. Although the overall magnitude is similar to that observed in SrFe$_2$As$_2$ [16] the anisotropy is qualitatively different. In our case the low temperature Curie–Weiss tail is isotropic, and thus could originate from an impurity contribution. The isotropic behavior above the transition is more consistent with that observed in BaFe$_2$As$_2$ [14].

\[
\rho(300 \text{ K})/\rho(4 \text{ K}) = 10
\]

The role of trace amounts of ferromagnetic impurity phases such as Fe$_2$As [25], will be studied in more detail to determine the intrinsic behavior of the susceptibility. Finally, whether the current samples are affected by Sn substitution as suggested for single crystals of BaFe$_2$As$_2$ grown by a similar technique [14] must still be investigated.

We have synthesized single crystals of CaFe$_2$As$_2$, which possesses a first order transition at 170 K, which is likely a combined structural and magnetic transition. Given that superconductivity has been found by doping the isostructural Ba and Sr compounds [13, 18, 19] we believe that the Ca compound is also a likely candidate for the presence of superconductivity upon chemical substitution.

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