Anisotropic thermal expansion of Fe$_{1.06}$Te and FeTe$_{0.5}$Se$_{0.5}$ single crystals

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Abstract

Heat capacity and anisotropic thermal expansion was measured for Fe$_{1.06}$Te and FeTe$_{0.5}$Se$_{0.5}$ single crystals. Previously reported phase transitions are clearly seen in both measurements. In both cases the thermal expansion is anisotropic. The uniaxial pressure derivatives of the superconducting transition temperature in FeTe$_{0.5}$Se$_{0.5}$ inferred from the Ehrenfest relation have opposite signs for in-plane and c-axis pressures. Whereas the Grüneisen parameters for both materials are similar and only weakly temperature-dependent above $\sim 80$ K, at low temperatures (in the magnetically ordered phase) the magnetic contribution to the Grüneisen parameter in Fe$_{1.06}$Te is significantly larger than electron and phonon contributions combined.

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The discovery of superconductivity in F-doped LaFeAsO and K-doped BaFe$_2$As$_2$ compounds caused an increased interest in studies of the materials containing Fe-As layers as a structural unit. More recently superconductivity was reported in two other structural families that have iron-pnictogen, or iron-chalcogen layers in their structure, Li$_{1-x}$FeAs$^3$ and FeSe$_{1-x}$.$^4$ For the latter material, an enhancement of superconducting transition temperature, $T_c$, was observed upon substitution of S or Te for Se.$^5$ Recently, large single crystals of the Fe$_{1+y}$Te$_x$Se$_{1-x}$ were grown and explored.$^6$

Thermal expansion is professed to be uniquely sensitive to magnetic, structural and superconducting transitions.$^7$ Anisotropic thermal expansion measurements in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ $^{8,9,10}$ have been instrumental in inferring unusually large, anisotropic, uniaxial pressure derivatives of superconducting transition temperature, $T_c$, in these compounds. Grüneisen parameter analysis on the other hand is frequently used for comparative, thermodynamic studies of related materials.$^{11}$ To gain more understanding about the members of the Fe$_{1+y}$Te$_x$Se$_{1-x}$ family, in this work we present the measurements of heat capacity and anisotropic thermal expansion on its two members: non-superconducting, parent compound, Fe$_{1.06}$Te, and, close to optimally doped, superconducting, FeTe$_{0.5}$Se$_{0.5}$.

Single crystals of Fe$_{1.06}$Te, and FeTe$_{0.5}$Se$_{0.5}$ were grown by Bridgeman technique. Detailed description of the crystal growth procedure and compositional analysis for these samples can be found elsewhere.$^6$ The heat capacity of the samples was measured using a hybrid adiabatic relaxation technique of the heat capacity option in a Quantum Design, PPMS-14 instrument. Thermal expansion data were obtained using a capacitive dilatometer constructed of OFHC copper; a detailed description of the dilatometer is presented elsewhere.$^{12}$ The dilatometer was mounted in a Quantum Design PPMS-14 instrument and was operated over a temperature range of 1.8 to 305 K. The samples were cut and lightly (and carefully) polished so as to have parallel surfaces parallel and perpendicular to the $c$-direction with the distances $L$ between the surfaces ranging between approximately $0.3 - 1.4$ mm. Specific heat and thermal expansion data were taken on warming and on the same samples.

Thermodynamic properties of materials are frequently analyzed using the concept of a Grüneisen function (or a Grüneisen parameter)$^{13}$. For a single energy scale, $\varepsilon$, the Grüneisen parameter, $\gamma$, is defined as $\gamma = -d \ln \varepsilon / d \ln V$, where $V$ is a molar volume. Using thermodynamic relations, we can obtain $\gamma(T, V) = \beta V / \chi_s C_p$, where $\beta$ is a volume thermal expansion
coefficient \( \beta = (\partial \ln V / \partial T)_P \), \( \chi_S \) is an adiabatic compressibility \( (\chi_S = -(\partial \ln V / \partial P)_S) \) and \( C_p \) is a heat capacity at a constant pressure. If, as in many modern materials of interest, more than one contribution to the thermodynamic properties is present (e.g. vibrational, electronic, magnetic, etc.), the Grüneisen parameters are not additive, rather the Grüneisen parameter for the material is an average, weighted by the heat capacity contribution of each component:

\[
\gamma = \frac{\sum \gamma_r C_r}{\sum C_r}
\]

Even with such complexity, the Grüneisen parameter behavior in many cases still allows for some qualitative conclusions.

Sometimes, in the analysis of experimental data, lacking the temperature-dependent compressibility data, the temperature dependence of the Grüneisen parameter can be approximated as being proportional to \( \beta/C_p \) under the assumption that the relative temperature dependence of \( \chi_S \) is significantly smaller than that of thermal expansion coefficient or heat capacity. We will follow such approach in this work.

The temperature-dependent heat capacity data for the Fe\(_{1.06}\)Te crystal are shown in Fig. 1. A narrow, sharp peak is clearly seen at \( \sim 68 \) K. The electronic specific heat coefficient is estimated as \( \gamma \approx 34 \) mJ/mol K\(^2\). These data are very similar to those reported for Fe\(_{1.05}\)Te in Ref. 14. The transition (in Fe\(_{1.068}\)Te) was identified as being first order, structural and antiferromagnetic. The temperature-depending anisotropic thermal expansivities and thermal expansion coefficients for Fe\(_{1.06}\)Te are shown in Fig. 2. The thermal expansion coefficients are less anisotropic than in BaFe\(_2\)As\(_2\). The c-axis thermal expansion coefficient is positive and almost temperature independent above the transition and small, negative, weakly temperature-dependent below the transition. The transition is seen as a sharp feature in each of the measurements. The length in the ab plane decreases, in relative terms, by \( \approx 4.4 \cdot 10^{-3} \) on cooling through the transition. The change along the c-axis is smaller and of the opposite sign: the relative increase along the c-axis is \( \approx 9 \cdot 10^{-4} \). We note, however, that the ”bulk” thermal expansion measurements yield an average thermal expansion and are not sensitive to possible change in structural symmetry in different phases. Moreover, in the current measurements the exact in-plane direction was not defined. The thermal expansivities are in remarkable agreement with those measured by neutron powder diffraction for Fe\(_{1.076}\)Te in Ref. 15 (Fig. 2). The change at the transition in the c-axis is very close to the value reported by neutron scattering (between 80 K and 5 K)\(^{16}\), Our in-plane data are within the range of that from neutron scattering\(^{16}\) but not the same as reported change in
either \(a\) or \(b\) lattice parameter, that is not surprising considering that our measurements were done for arbitrary in-plane orientation and that there is a possibility of in-plane structural domains below the structural/magnetic transition that will cause some average value to be measured by ”bulk” dilatometric techniques.

The temperature-dependent heat capacity for FeTe\(_{0.5}\)Se\(_{0.5}\) crystal is shown in Fig. 3. A feature associated with a superconducting transition (with an onset \(T_{c}^{onset} \approx 14\) K) is clear in the data. Thermal expansion of the FeTe\(_{0.5}\)Se\(_{0.5}\) crystal (Fig. 4) is more anisotropic that that of Fe\(_{1.06}\)Te. The in-plane thermal expansion is negative below \(\sim 120\) K. The features at the superconducting transition are seen in both directions and the changes in the thermal expansion at \(T_{c}\) are of the opposite sign in the in-plane and \(c\)-axis data sets.

The initial uniaxial pressure derivatives of \(T_{c}\) can be estimated using the Ehrenfest relation for the second order phase transitions\(^{11}\):

\[
dT_c/dp_i = \frac{V_m \Delta \alpha_i}{\Delta C_p/T_c}
\]

where \(V_m\) is the molar volume, \(\Delta \alpha_i\) is a change of the linear \((i = ab, c)\) thermal expansion coefficient at the superconducting transition, and \(\Delta C_p/T_c\) is a change of the specific heat at the superconducting transition divided by \(T_c\). Using experimental values: \(V_m = 0.26 \cdot 10^{-4}\) m\(^3\)/mol, \(\Delta \alpha_{ab} \approx -1.8 \cdot 10^{-6}\) K\(^{-1}\), \(\Delta \alpha_c \approx 0.8 \cdot 10^{-6}\) K\(^{-1}\), and \(\Delta C_p/T_c \approx 13.4\) mJ/mol K\(^2\), we can estimate initial uniaxial pressure derivatives of the superconducting transition temperature in FeTe\(_{0.5}\)Se\(_{0.5}\): \(dT_c/dp_{ab} \approx -0.35\) K/kbar, \(dT_c/dp_c \approx 0.16\) K/kbar. This rough estimate of the hydrostatic pressure derivative of \(T_{c}\) is then \(dT_c/dP \approx 2 \cdot dT_c/dp_{ab} + dT_c/dp_c \approx -0.54\) K/kbar. So in-plane pressure should cause a decrease of \(T_{c}\) and pressure along the \(c\)-axis is expected to cause an increase of \(T_{c}\). The signs of the inferred uniaxial pressure derivatives are the same as for ”underdoped” Ba(Fe\(_{0.962}\)Co\(_{0.038}\))\(_2\)As\(_2\), but the absolute values are more moderate; about an order of magnitude smaller.

The temperature-dependent Grüneisen parameters, in the form of \(\beta/C_p\), (volume thermal expansion, \(\beta\), is defined here as \(\beta = 2 \cdot \alpha_{ab} + \alpha_c\)) for Fe\(_{1.06}\)Te and FeTe\(_{0.5}\)Se\(_{0.5}\) are shown in Fig. 5 (The excessive noise below \(\sim 5\) K could be caused by the division by small \(C_p\) values.) For FeTe\(_{0.5}\)Se\(_{0.5}\) the \(\beta/C_p\) is practically temperature-independent above \(\sim 15\) K. For Fe\(_{1.06}\)Te the value of \(\beta/C_p\) at temperatures above the structural/magnetic phase transition is very close to that of FeTe\(_{0.5}\)Se\(_{0.5}\), however below the transition the Grüneisen parameter of Fe\(_{1.06}\)Te is significantly higher, and, close to the transition is only weakly
temperature-dependent. Most probably this difference is due to the magnetic contribution (the heat capacity and the inferred Debye temperature are continuous if the region around transition is excluded, so probably the change in the phonon term is not so drastic through the transition) however other contributions cannot be excluded and more studies are required to clarify this issue.

In summary, thermal expansion of Fe$_{1.06}$Te and FeTe$_{0.5}$Se$_{0.5}$ is anisotropic, phase transitions are clearly seen. The signs of the inferred uniaxial pressure derivatives of $T_c$ in FeTe$_{0.5}$Se$_{0.5}$ are opposite for in-plan ($dT_c/dp_{ab} < 0$) and c-axis ($dT_c/dp_c > 0$) pressures. The Grüneisen parameters for both materials are similar and only weakly temperature-dependent above $\sim 80$ K. At low temperatures (in the magnetically ordered phase) the magnetic contribution to the Grüneisen parameter in Fe$_{1.06}$Te appears to be significantly larger than electron and phonon contributions combined.

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FIG. 1: Temperature-dependent heat capacity of Fe$_{1.06}$Te single crystal. Left inset: enlarged region near the structural/magnetic phase transition; right inset: low temperature part of the heat capacity plotted as $C_p/T$ vs. $T^2$. 
FIG. 2: (Color online) Anisotropic thermal expansivities (lower panel) and thermal expansion coefficients (upper panel) of Fe$_{1.06}$Te single crystal. Inset to the upper panel: enlarged region near the structural/magnetic phase transition. Symbols: normalized at $T = 150$ K data for Fe$_{1.076}$Te taken from Ref. 15.
FIG. 3: Temperature-dependent heat capacity of FeTe$_{0.5}$Se$_{0.5}$ single crystal. Inset: enlarged region near the superconducting transition transition plotted as $C_p/T$ vs. $T$. Lines show how $\Delta C_p/T_c$ value is defined.
FIG. 4: (Color online) Anisotropic thermal expansion coefficients of FeTe$_{0.5}$Se$_{0.5}$ single crystal. Inset: enlarged region near the superconducting transition transition. Lines show how $\Delta \alpha_i$ values are defined.
FIG. 5: (Color online) Grüneisen parameters, $\beta/C_p$, of Fe$_{1.06}$Te and FeTe$_{0.5}$Se$_{0.5}$ single crystal.