PHYSICAL REVIEW B **80**, 134523 (2009)

Anisotropic thermal expansion of $Fe_{1.06}Te$ and $FeTe_{0.5}Se_{0.5}$ single crystals

S. L. Bud'ko and P. C. Canfield
Ames Laboratory, U.S. DOE and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA

A. S. Sefat, B. C. Sales, M. A. McGuire, and D. Mandrus
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

(Received 21 July 2009; revised manuscript received 7 October 2009; published 28 October 2009)

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. The Grüneisen parameters for both materials are similar and only weakly temperature dependent above ~80 K.

DOI: 10.1103/PhysRevB.80.134523 PACS number(s): 65.40.Ba, 65.40.De, 74.25.Bt, 74.62.Fj

The discovery of superconductivity in F-doped LaFeAsO (Ref. 1) and K-doped $BaFe_2As_2$ (Ref. 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, $Li_{1-x}FeAs$ (Ref. 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 $Fe_{1+y}Te_xSe_{1-x}$ 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 $Ba(Fe_{1-x}Co_x)_2As_2$ (Refs. 8–10) 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 $Fe_{1+y}Te_xSe_{1-x}$ family, in this work we present the measurements of heat capacity and anisotropic thermal expansion on its two members: nonsuperconducting, 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. Having in mind the softness and somewhat micaceous morphology of the samples as well rather small changes in thermal expansion coefficients at the superconducting transitions for the $FeTe_{0.5}Se_{0.5}$ crystal (see below), the error bars for the estimates of the uniaxial pressure derivatives of the superconducting transition temperature may be as high as ~30%, that still allows for a semiquantitative analysis of the results.

Thermodynamic properties of materials are frequently analyzed using the concept of a Grüneisen function (or a Grüneisen parameter).[11] For a single energy scale, ε, the Grüneisen parameter, γ, 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 β is a volume thermal expansion coefficient $[\beta = (\partial \ln V / \partial T)_P]$, χ_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:[11] $\gamma = \Sigma_r \gamma_r C_r / \Sigma_r C_r$. 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[13] as being proportional to β / C_p under the assumption that the relative temperature dependence of χ_S is significantly smaller then 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 ~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[16] as being first order, structural (high-temperature tetragonal to low-temperature monoclinic), 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 $BaFe_2As_2$.[8] The *c*-axis thermal expansion coefficient is positive and al-

©2009 The American Physical Society

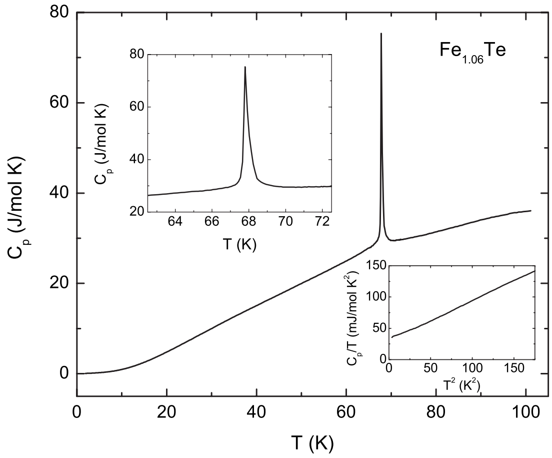

FIG. 1. Temperature-dependent heat capacity of $Fe_{1.06}Te$ single crystal. Left inset: enlarged region near the structural/magnetic phase transition; right inset: low-temperature part of the heat capacity plotted as C_p/T vs T^2.

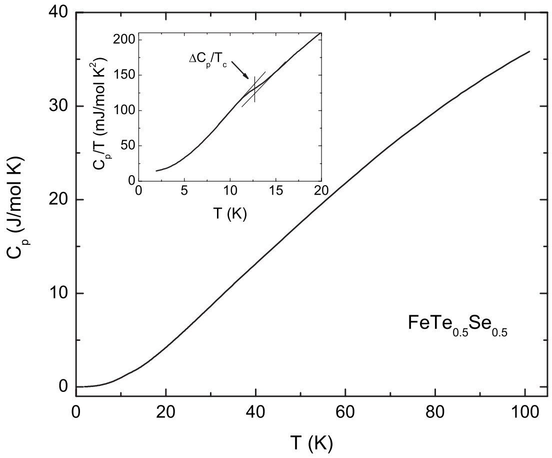

FIG. 3. Temperature-dependent heat capacity of $FeTe_{0.5}Se_{0.5}$ single crystal. Inset: enlarged region near the superconducting transition plotted as C_p/T vs T. Lines show how $\Delta C_p/T_c$ value is defined.

most 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 $\approx 4.4 \times 10^{-3}$ 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 $\approx 9 \times 10^{-4}$. We note, however, that the "bulk" thermal expansion measurements yield an average (of some intermediate value) 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 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, intermediate, value to be measured by "bulk" dilatometric techniques.

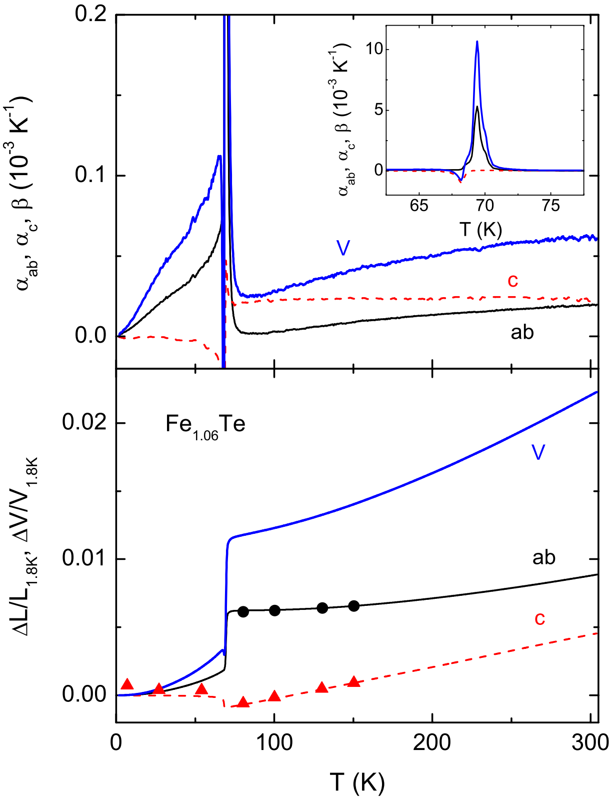

FIG. 2. (Color online) Anisotropic thermal expansivities (lower panel) and thermal expansion coefficients (upper panel) of $Fe_{1.06}Te$ single crystal. Inset to the upper panel: enlarged region near the structural/magnetic phase transition. Symbols: normalized at $T = 150$ K data for $Fe_{1.076}Te$ taken from Ref. 15.

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 than that of $Fe_{1.06}Te$. The in-plane thermal expansion is negative below ~ 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 in the linear $(i = ab, c)$ thermal expansion coefficient at the superconducting transition, and $\Delta C_p/T_c$ is a change in the specific heat at the superconducting transition divided by T_c. Using experi-

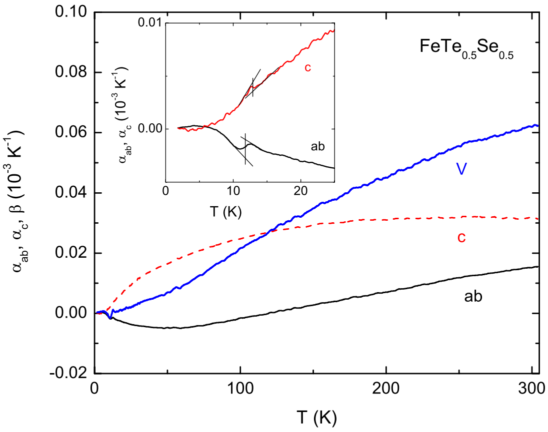

FIG. 4. (Color online) Anisotropic thermal expansion coefficients of FeTe$_{0.5}$Se$_{0.5}$ single crystal. Inset: enlarged region near the superconducting transition. Lines show how $\Delta\alpha_i$ values are defined.

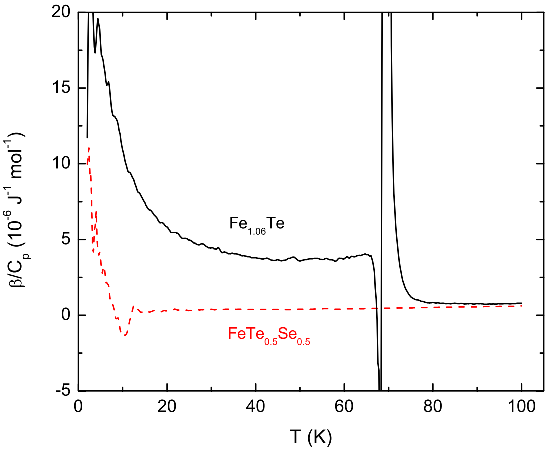

FIG. 5. (Color online) Grüneisen parameters, β/C_p, of Fe$_{1.06}$Te and FeTe$_{0.5}$Se$_{0.5}$ single crystals.

mental values: $V_m = 0.26\times10^{-4}$ m^3/mol,[6] $\Delta\alpha_{ab}\approx -1.8\times10^{-6}$ K^{-1}, $\Delta\alpha_c \approx 0.8\times10^{-6}$ 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 and $dT_c/dp_c \approx 0.16$ 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 in T_c and pressure along the c axis is expected to cause an increase in 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$_2$,[8] but the absolute values are more moderate; about an order of magnitude smaller.

The temperature-dependent Grüneisen parameters, in the form of β/C_p, (volume thermal expansion, β, 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 ~5 K could be caused by the division by small C_p values.) For FeTe$_{0.5}$Se$_{0.5}$ the β/C_p is practically temperature-independent above ~15 K. For Fe$_{1.06}$Te the value of β/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, such as domain formation accompanying the structural transitions, 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-plain ($dT_c/dp_{ab}<0$) and c-axis ($dT_c/dp_c>0$) pressures. The Grüneisen parameters for both materials are similar and only weakly temperature dependent above ~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.

Work at the Ames Laboratory was supported by the U.S. Department of Energy—Basic Energy Sciences under Contract No. DE-AC02-07CH11358. Research at Oak Ridge National Laboratory was sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy. We are indebted to George M. Schmiedeshoff for his help in establishing dilatometry technique in Ames Laboratory Novel Materials and Ground States Group and for many propitious advices. M. T. C. Apoo is gratefully acknowledged.

---

[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).
[2] M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. **101**, 107006 (2008).
[3] X. C. Wang, Q. Q. Liu, Y. X. Lv, W. B. Gao, L. X. Yang, R. C. Yu, F. Y. Li, and C. Q. Jin, Solid State Commun. **148**, 538 (2008).
[4] F.-C. Hsu, J.-Y. Luo, K.-W. Yeh, T.-K. Chen, T.-W. Huang, P. M. Wu, Y.-C. Lee, Y.-L. Huang, Y.-Y. Chu, D.-C. Yan, and M.-K. Wu, Proc. Natl. Acad. Sci. U.S.A. **105**, 14262 (2008).
[5] Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, and Y. Takano, Appl. Phys. Lett. **94**, 012503 (2009).
[6] B. C. Sales, A. S. Sefat, M. A. McGuire, R. Y. Jin, D. Mandrus, and Y. Mozharivskyj, Phys. Rev. B **79**, 094521 (2009).
[7] F. Kromer, R. Helfrich, M. Lang, F. Steglich, C. Langhammer, A. Bach, T. Michels, J. S. Kim, and G. R. Stewart, Phys. Rev. Lett. **81**, 4476 (1998).
[8] S. L. Bud'ko, N. Ni, S. Nandi, G. M. Schmiedeshoff, and P. C. Canfield, Phys. Rev. B **79**, 054525 (2009).
[9] F. Hardy, P. Adelmann, T. Wolf, H. v. Löhneysen, and C. Meingast, Phys. Rev. Lett. **102**, 187004 (2009).
[10] M. S. da Luz, J. J. Neumeier, R. K. Bollinger, A. S. Sefat, M. A.

McGuire, R. Jin, B. C. Sales, and D. Mandrus, Phys. Rev. B **79**, 214505 (2009).

[11] T. H. K. Barron and G. K. White, *Heat Capacity and Thermal Expansion at Low Temperatures* (Kluwer Academic, New York/Plenum, New York, 1999).

[12] G. M. Schmiedeshoff, A. W. Lounsbury, D. J. Luna, S. J. Tracy, A. J. Schramm, S. W. Tozer, V. F. Correa, S. T. Hannahs, T. P. Murphy, E. C. Palm, A. H. Lacerda, S. L. Bud'ko, P. C. Canfield, J. L. Smith, J. C. Lashley, and J. C. Cooley, Rev. Sci. Instrum. **77**, 123907 (2006).

[13] R. Pott, R. Schefzyk, D. Wohlleben, and A. Junod, Z. Phys. B: Condens. Matter **44**, 17 (1981).

[14] G. F. Chen, Z. G. Chen, J. Dong, W. Z. Hu, G. Li, X. D. Zhang, P. Zheng, J. L. Luo, and N. L. Wang, Phys. Rev. B **79**, 140509(R) (2009).

[15] Wei Bao, Y. Qiu, Q. Huang, M. A. Green, P. Zajdel, M. R. Fitzsimmons, M. Zhernenkov, S. Chang, Minghu Fang, B. Qian, E. K. Vehstedt, Jinhu Yang, H. M. Pham, L. Spinu, and Z. Q. Mao, Phys. Rev. Lett. **102**, 247001 (2009).

[16] Shiliang Li, Clarina de la Cruz, Q. Huang, Y. Chen, J. W. Lynn, Jiangping Hu, Yi-Lin Huang, Fong-Chi Hsu, Kuo-Wei Yeh, Maw-Kuen Wu, and Pengcheng Dai, Phys. Rev. B **79**, 054503 (2009).