Thermal expansion of RFeAsO (R=La,Ce,Pr,Sm,Gd)

R. Klingeler, L. Wang, U. Köhler, G. Behr, C. Hess, B. Büchner
Institute for Solid State Research, IFW Dresden, D-01171 Dresden, Germany
E-mail: r.klingeler@ifw-dresden.de

Abstract. We present measurements of the thermal expansion coefficient $\alpha$ of polycrystalline RFeAsO (R = La,Ce,Pr,Sm,Gd). Anomalies at the magnetic ordering transitions indicate a significant magneto-elastic coupling and a negative pressure dependence of $T_N$. The structural transitions are associated by large anomalies in $\alpha$. Rare earth magnetic ordering in CeFeAsO, PrFeAsO, and SmFeAsO yields large positive anomalies at low temperatures.

Layered Fe$_2$As$_2$-materials have raised enormous attention due to the discovery of superconductivity with transition temperatures $T_C$ up to 28 K in LaFeAsO$_{1-x}$F$_x$. Upon substitution of La by rare earths, $T_C$ is increased to above 50 K. Interestingly, evolution of superconductivity is associated to the suppression of a magnetically ordered orthorhombic phase, which has been found in the undoped parent compound. In RFeAsO, both tetragonal distortion and magnetic ordering are observed at intermediate temperatures around $\sim 150$ K. A spin density wave (SDW)-type of antiferromagnetic order evolves slightly below the temperature $T_S$ of orthorhombic distortion of the tetragonal high temperature phase.

Here, we present thermal expansion data of polycrystalline RFeAsO with R = La,Ce,Pr,Sm,Gd. Our measurements yield a very sensitive measure of the volume changes of the materials. We find clear anomalies of the coefficient of linear thermal expansion $\alpha$ at the structural and magnetic transitions, i.e. at $T_S$ and $T_N$, respectively. It has been shown earlier for LaFeAsO, that anomalous contributions to $\alpha$ are visible far above $T_S$. Similar effects are found in RFeAsO with R = Ce,Pr,Sm,Gd. In addition, magnetic ordering of the rare earth moments is accompanied by low temperature anomalies of the thermal expansion coefficient.

Preparation and characterization of the polycrystalline samples has been described in Ref. [12]. The crystal structure and the composition were confirmed by powder x-ray diffraction. In addition, our samples have been characterized by means of specific heat, magnetization, transport, and $\mu$SR experiments. For the thermal expansion measurement a three-terminal capacitance dilatometer was utilized, which allows an accurate study of sample length changes. We measured the macroscopic length $L(T)$ of the samples and calculated the coefficient of linear thermal expansion $\alpha = 1/L \cdot dL/dT$, which is the first temperature derivative of $L(T)$. For our polycrystalline samples the volume expansion coefficient $\beta$ is given as $\beta = 3\alpha$.

Figure 1 shows the linear thermal expansion coefficient $\alpha$ of RFeAsO with R=La,Ce,Pr,Sm,Gd, between 5 K and 250 K. For all R (except Pr), the thermal expansion coefficient exhibits two huge anomalies with opposite sign. The anomalies in $\alpha(T)$ can be attributed to the structural and SDW transitions of the compound. The transition temperatures determined from the positions of the extrema are marked by the dashed lines and are listed in Table 1.
Figure 1. Temperature dependence of the coefficient of linear thermal expansion, $\alpha(T)$, of RFeAsO (R = La, Ce, Pr, Sm, Gd). Two anomalies indicated by the dashed lines are associated to a structural distortion at $T_S$ and SDW-formation at $T_N$. For PrFeAsO, no clear anomaly can be attributed to $T_N$. The arrow indicates $T_N^{Pr,\mu}$ taken from $\mu$SR data. [10]
Table 1. Magnetic and structural transition temperatures of RFeAsO with R = La,Ce,Pr,Sm,Gd as deduced from Figures 1 and 2. For comparison, transition temperatures from $\mu$SR (Ref. [10]) and resistivity studies (Ref. [12]) are listed, too.

| R    | $T_N$       | $T_S$       | $T^R_N$ | $T^\mu_N$ | $T^\rho_S$ | $T^R_N$ |
|------|-------------|-------------|---------|-----------|------------|---------|
| La   | (137±1) K   | (157±1) K   | -       | 139 K     | 158 K      | -       |
| Ce   | (134±2) K   | (148±2) K   | $\lesssim$ 5 K | 137 K | 151 K | 4.4 K |
| Pr   | (147±5) K   | (11.3±0.3) K | 123 K   | 136 K     | 11 K       |         |
| Sm   | (136±2) K   | (148±5) K   | $\lesssim$ 5 K | 138 K | 160 K | 4.7 K |
| Gd   | (128±2) K   | (136±5) K   | -       | -         | -          | -       |

The SDW formation at $T_N$ generates negative anomalies in the thermal expansion coefficients. Note, that for PrFeAsO the SDW-anomaly is not visible although the onset of magnetic order at $T^\mu_N = 137$ K has been demonstrated in $\mu$SR studies. [10] According to the Ehrenfest relation, the negative anomalies in $\alpha(T)$ at $T_N$ qualitatively imply a negative hydrostatic pressure dependence of $T_N$. This finding is in agreement with resistivity studies on LaFeAsO. [14] The anomalies in $\alpha$ at $T_N$ indicate a strong coupling of the magnetic transition to the crystal lattice. However, the shape of the anomalies deviates from what is expected for second-order phase transitions, probably due to the closeness to $T_S$.

In contrast, the structural transition at $T_S$ gives rise to a positive anomaly in $\alpha$. Remarkably, this anomaly is very broad, extending to temperatures far above $T_S$. In particular, it has been shown previously for LaFeAsO that the anomalous contributions to $\alpha$ extend to significantly higher temperatures than the corresponding anomalies found in specific heat, magnetization, and resistivity. The enhanced $\alpha$ suggests the presence of strong fluctuations preceding the structural transitions at $T_S$. So far, the origin of these fluctuations is unknown. One might attribute them to a competing instability in vicinity of the actual ground state. A possible scenario is a competing orthomagnetic phase which was suggested in Ref. [15]. In this scenario, long range order of the competing magnetic phase is hindered by the orthorhombic distortion, whereas the increase of the corresponding anomalous positive contribution to the thermal expansion coefficient is truncated by the structural transition at $T_S$.

In the materials with magnetic R-sites, magnetic ordering of the rare earth moments is found (see, e.g., [16, 17, 10]). The evolution of rare earth magnetic order is accompanied by strong volume changes. Coupling of magnetic and lattice degrees of freedom is clearly visible in fig. 2 For PrFeAsO, there is a pronounced peak of the thermal expansion coefficient at $T^\mu_{Pr} = (11.3\pm0.3)$ K. The observed ordering temperature agrees to previous neutron and $\mu$SR data. [16] [10]. Qualitatively, the strong positive anomaly implies a positive hydrostatic pressure dependence of $T^\mu_{Pr}$. Also for CeFeAsO and SmFeAsO, the data in fig. 2 indicate a strong positive anomaly in $\alpha$ slightly below 5 K, which is the lower temperature limit of our device. In contrast, no anomaly is seen for GdFeAsO. Note, that magnetic R-site ordering occurs in our samples at $T^C_{Ce,\mu} = 4.4$ K, $T^S_{Sm,\mu} = 4.7$ K, and $T^G_{Gd} = 3.7$ K. [10].

In conclusion, our thermal expansion studies have been shown being a sensitive probe for structural changes as well as Fe and rare earth magnetic ordering in RFeAsO (R = La,Ce,Pr,Sm,Gd). The magnetic and structural ordering phenomena are associated to large anomalies in $\alpha$, which allow to determine the phase diagram. Our data imply a negative pressure dependence of the Fe-ordering transition and a positive one for Pr,Ce, and Sm ordering. Strong fluctuations at $T \gg T_S$ indicate a competing, possibly magnetic instability to the ground state.
Figure 2. Temperature dependence of the coefficient of linear thermal expansion, $\alpha(T)$, of RFeAsO ($R = \text{Ce,Pr,Sm,Gd}$) at temperatures below $T = 20\,\text{K}$ where magnetic ordering of the rare earth moments is expected. Note, that the experimental setup provides data for $T \geq 5\,\text{K}$, i.e. the complete anomaly is only visible for PrFeAsO which exhibits $T_N^{\text{Pr}} = 11.3\,\text{K}$.

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