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Contamination from magnetic starting materials in flux-grown single crystals of RFeAsO superconductors

J.-Q. Yan
Iowa State University

Qingfeng Xing
Iowa State University, qxing@ameslab.gov

Brandt A. Jensen
Iowa State University, brandtj@iastate.edu

H. Xu
Iowa State University

Kevin W. Dennis
Iowa State University, dennis@ameslab.gov

See next page for additional authors

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Abstract
While the flux growth often provides the best method for obtaining single crystals of new-novel materials, the process is prone to producing crystals with trapped second-phase inclusions. In the case of NdFeAsO single crystals grown out of NaAs flux under ambient pressure, some crystals show a lambda anomaly in the specific heat curve at ~12 K. This anomaly is missing in other crystals from the same batch. We show that the lambda anomaly at 12 K is from residual NdAs starting material which is mainly on the edges of the crystals. The isothermal magnetization of LaFeAsO at 300 K clearly illustrates the effect of ferromagnetic impurities on the magnetic properties of LaFeAsO crystals.

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Authors
J.-Q. Yan, Qingfeng Xing, Brandt A. Jensen, H. Xu, Kevin W. Dennis, R. William McCallum, and Thomas A. Lograsso

Contamination from magnetic starting materials in flux-grown single crystals of *R*FeAsO superconductors

J.-Q. Yan,[1,*] Q. Xing,[1] B. Jensen,[1] H. Xu,[1,2] K. W. Dennis,[1] R. W. McCallum,[1,3] and T. A. Lograsso[1]
[1]*Division of Materials Science and Engineering, Ames Laboratory, US-DOE, Ames, Iowa 50011, USA*
[2]*Institute of Materials Science, Shanghai University, Shanghai 200072, People's Republic of China*
[3]*Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, USA*
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While the flux growth often provides the best method for obtaining single crystals of new-novel materials, the process is prone to producing crystals with trapped second-phase inclusions. In the case of NdFeAsO single crystals grown out of NaAs flux under ambient pressure, some crystals show a lambda anomaly in the specific heat curve at ∼12 K. This anomaly is missing in other crystals from the same batch. We show that the lambda anomaly at 12 K is from residual NdAs starting material which is mainly on the edges of the crystals. The isothermal magnetization of LaFeAsO at 300 K clearly illustrates the effect of ferromagnetic impurities on the magnetic properties of LaFeAsO crystals.

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The discovery in 2008 of the superconductivity in $LaFeAsO_{1-x}F_x$ with the superconducting transition temperature of 26 K has attracted extensive interest of physicists, chemists, and materials scientists.[1] Much effort has been devoted to growing sizable single crystals to explore the intrinsic and anisotropic physical properties of this new superconductor. High-quality *R*FeAsO (R = rare earth) single crystals of submillimeter size were first grown out of NaCl flux under ambient or high pressure.[2–5] Later, NaAs flux was employed to successfully grow millimeter-sized single crystals under ambient pressure.[6] The larger crystals, with a typical size of $3 \times 4 \times 0.05 \sim 0.3$ mm^3, have enabled the study of peculiar physical properties of this new family of superconductors with various techniques including neutron scattering.[7–10]

The crystal growth in NaAs flux generally employs NaAs, *R*As, Fe_2O_3, and Fe as starting materials. Among them, Fe_2O_3, Fe, and some of the *R*As binaries all exhibit ferro- or antiferromagnetic ordering. The magnetic properties of *R*As compounds have been well studied.[11] Antiferromagnetic order has been observed in CeAs, NdAs, and GdAs at 7 K, 11 K, and 25 K, respectively. These magnetic starting materials can be trapped in the crystals as inclusions and/or intergrowths or adhere to the surface, thus affecting the measured properties of the single crystals. As demonstrated by Johnston,[12] even a small amount of magnetic impurities can dramatically affect the measured magnetic properties of *R*FeAsO compounds. In this paper we report the magnetic properties of LaFeAsO and specific heat of NdFeAsO to illustrate how these magnetic impurities could affect the magnetic measurements and introduce extra features to the specific heat.

LaFeAsO and NdFeAsO single crystals were grown in a NaAs flux under ambient pressure. The starting materials are commercial Fe_2O_3 (99.99% Alfa Aesar) and Fe (99.9%, Alfa Aesar) powders, and locally prepared LaAs, NdAs, and NaAs. The synthesis of LaAs and NaAs as well as the crystal-growth process parameters can be found elsewhere.[6] NdAs was synthesized by firing As chunks and Nd filings sealed in a quartz tube under 1/3 atmosphere Ar gas at 565°C for 15 hours. NdAs was taken out of the quartz tube and thoroughly ground. Part of the powder was pelletized with a 1/4″ diameter die and then sealed in a quartz tube filled with 1/3 atmosphere Ar. The sealed quartz tube was heated to 1100°C over 12 hours, held at 1100°C for 12 hours, and then furnace cooled to room temperature. The magnetic properties and specific heat of NdAs were measured on this pellet for reasons described in the text. The temperature-dependent magnetic susceptibility and field-dependent magnetization were measured in a commercial, Quantum Design (QD) magnetic property measurement system (MPMS) magnetometer. The heat capacity data on the samples were measured using a hybrid adiabatic relaxation technique of the heat capacity option in a QD physical property measurement system (PPMS) instrument in the temperature range of 2 K ∼ 220 K. Typical of the FeAs-based superconductors, the platelike *R*FeAsO crystals are easy to cleave. Microstructural studies were performed with a JEOL JSM 6100 scanning electron microscope (SEM) to look for possible inclusions on cleaved surfaces, crystal surfaces, and edges. Energy-dispersive spectroscopy (EDS) was carried out with an Oxford Link Pentaset Detector.

Figure 1 shows the room-temperature powder x-ray diffraction pattern on crushed NdFeAsO single crystals. All reflections could be indexed with *P*4/*nmm* symmetry. No extra reflections from any starting materials were observed. Figure 2 shows the temperature dependence of specific heat of three different pieces of NdFeAsO single crystals grown from the same batch. Only the low-temperature range was displayed to highlight the difference at around 12 K. The specific heat data at around 150 K show identical features which correspond to the structural and magnetic orders. The anomaly at 6 K comes from the magnetic order of Nd ions, which has been confirmed by neutron scattering.[7] There is a clear difference between these three specific heat plots around 12 K. A well-defined lambda anomaly was observed for crystal no. 3, the magnitude of the lambda anomaly was much smaller for crystal no. 2, and it was barely observable for crystal no. 1. The ordering of Fe and Nd moments was studied with neutron single-crystal diffraction, and all three crystals show the same ordering temperatures. The

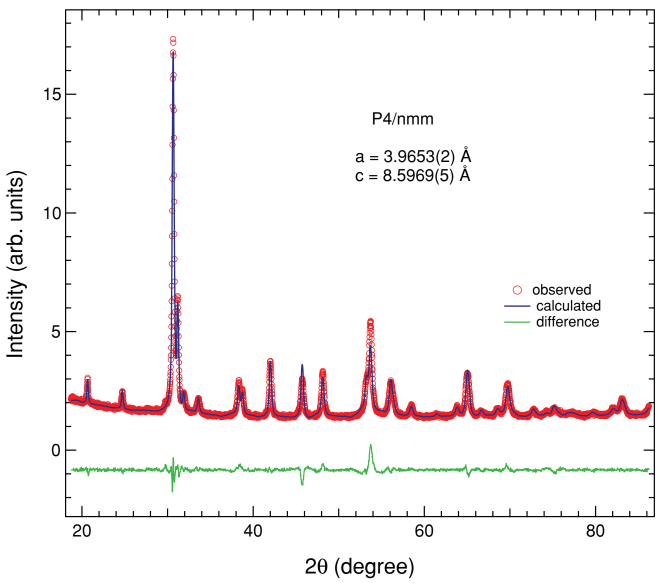

FIG. 1. (Color online) X-ray powder diffraction pattern from crushed NdFeAsO single crystals at room temperature obtained with monochromatic Cu K_α radiation. The pattern simulation was done with FullProf package.

temperature dependence of electrical resistivity did not show any observable difference at around 12 K. All evidence points to the fact that the lambda anomaly sitting at 12 K is from impurities.

Among all starting materials and other possible impurities, NdAs has been reported to order antiferromagnetically at 12 K. Thus we measured magnetization and specific heat of a polycrystalline NdAs pellet. The temperature dependence of magnetization confirmed that the NdAs synthesized in this study orders antiferromagnetically at 12 K, and the field dependence of magnetization at 5 K confirmed the

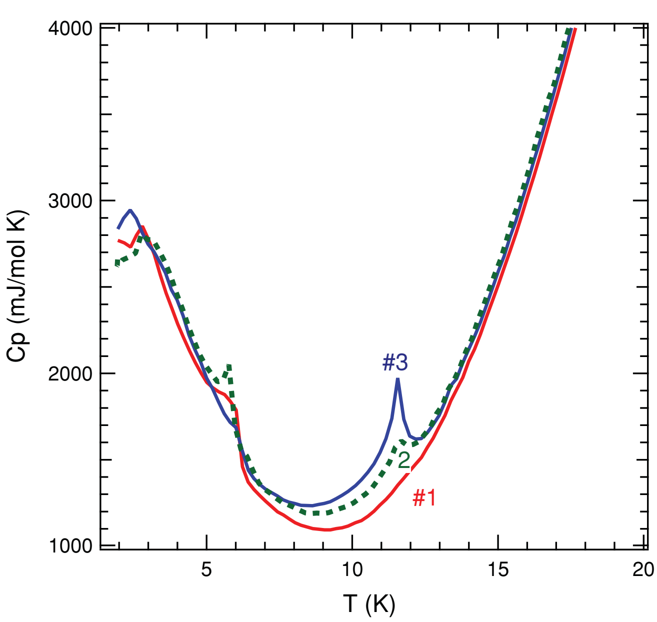

FIG. 2. (Color online) Temperature dependence of the specific heat of three different pieces of NdFeAsO single crystals grown from the same batch.

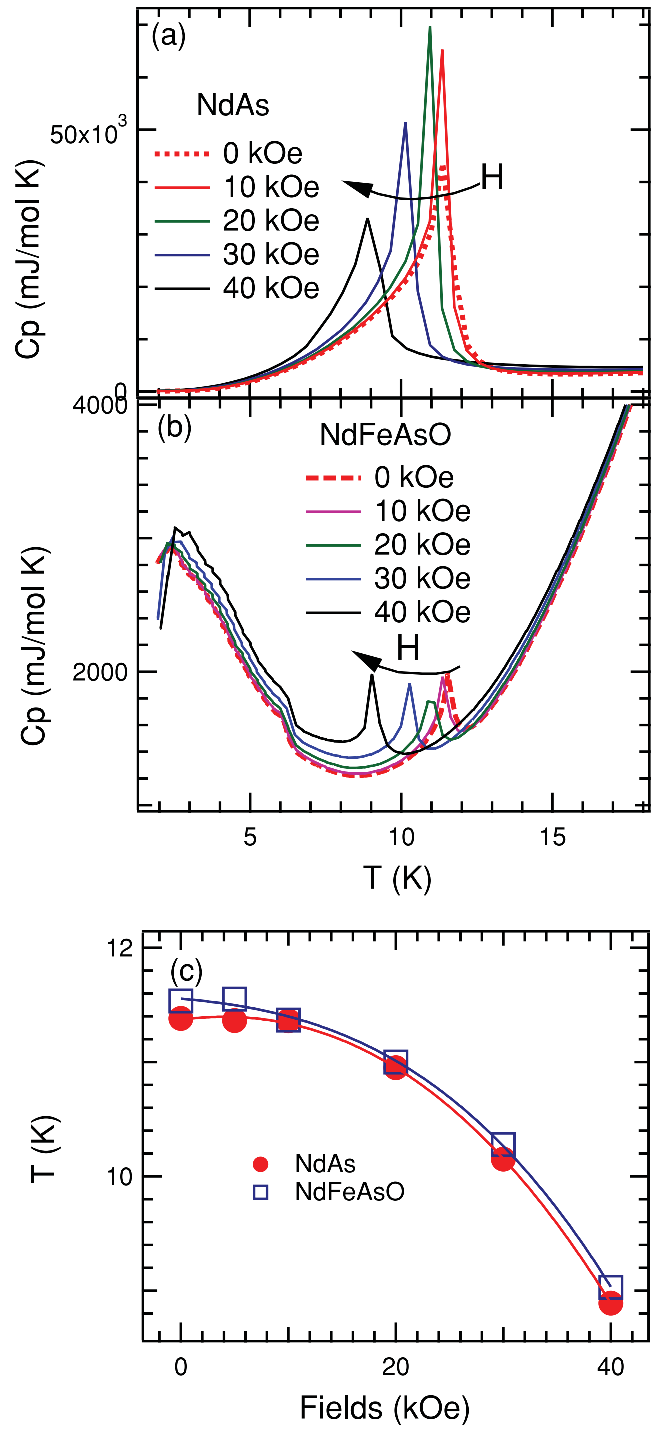

FIG. 3. (Color online) (a) Temperature dependence of the specific heat of polycrystalline NdAs under different magnetic fields. (b) Temperature dependence of the specific heat of NdFeAsO single crystal no. 3 under different magnetic fields. (c) Field dependence of a 12-K lambda anomaly in specific heat curves of polycrystalline NdAs and single-crystal NdFeAsO. The curves are a guide to eye.

metamagnetic transition at fields above 40 kOe.[13] Figure 3(a) shows the specific heat of NdAs under various magnetic fields. At zero external magnetic field, the lambda anomaly associated with the magnetic order could be well defined. With increasing magnetic field strength, the lambda anomaly shifts to the low-temperature side. The temperature dependence of magnetization measured under various external magnetic fields also confirmed the decrease of Neel temperature with increasing fields and gave the same field dependence. Figure 3(b) shows the field dependence of specific heat of the no. 3 NdFeAsO single crystal. A similar shift of the lambda anomaly to lower temperatures was observed with the increasing magnetic fields. If we simply define the peak position of lambda anomaly as the ordering temperature, as shown in Fig. 3(c), the ordering temperatures determined from Figs. 3(a) and 3(b) agree with each other very well. Thus the lambda anomaly at 12 K in the specific heat curve in Fig. 2 is from the magnetic order of the starting material NdAs.

This raises the question of where the residual NdAs is physically located. For flux-grown crystals, the impurities may be as physical inclusions within the crystal, incorporated into the lattice of crystals, or just adhered to the surface or edges of the crystals. To answer the above question, we examined the cleaved (001) surfaces with SEM. The cleaved surface is clean and the amount of NdAs as inclusion, if any, should be negligible. We then turned to examine the crystal surfaces for possible physically adhered impurities. After washing away NaAs flux and drying, we noticed that there is some residue on the surface of the crystals. We then cleaned the crystals with ultrasonic cleaning in acetone until the crystals were clean under an optical microscope. The specific heat was monitored before and after the ultrasonic cleaning, and no observable difference in magnitude or temperature dependence of the lambda anomaly was measured. We thus finally turned to look at the edges of the crystals. As shown in the upper inset of Fig. 4, a 10-μm-thick layer was observed on the edges of the NdFeAsO crystals. In this thin layer, some particles, which were determined with EDS to be TaAs, were surrounded by some very fine particles. The rough surface of the thin layer makes it difficult to accurately determine the composition of the fine particles. We suspect that magnetic impurities might stay in this thin layer. Since this thin layer stays after the ultrasonic cleaning, we therefore mechanically removed the thin layer with the aid of a surgical blade (see the lower inset of Fig. 4). As shown in Fig. 4, after removing the edges, no anomaly was observed at around 12 K in the temperature dependence of specific heat. This confirms that NdAs impurities are contained within the thin layer adhered to the edges of NdFeAsO single crystals. This amount of NdAs impurities could not be observed with regular laboratory x-ray diffraction experiments (see Fig. 1).

This thin layer may contain not only TaAs and NdAs, but other magnetic impurities such as Fe, Fe_2O_3, or other intermediate phases formed during the crystal growth.[14] The specific heat measurements discussed above are sensitive to the ordering of impurities within the measurement range but are insensitive to orderings which take place outside that temperature range. In order to investigate the possibility of magnetic impurity phases which order at higher temperatures, we have performed room-temperature magnetization measurements on LaFeAsO crystals grown from the same batch. One piece of the crystal with a layer of residue around the edges was intentionally selected, and the other piece without observable residue under an optical microscope was also measured for comparison. Figure 5 shows the field dependence of magnetization at room temperature of the above two LaFeAsO single crystals. Obviously, the crystal contaminated with the thin layer has a component to the magnetization which appears to saturate at high fields. Linear fits to the M(H) data for the field range H = 10–50 kOe were performed. The slope of the high-field linear fits gives the intrinsic susceptibility, and the H = 0 Oe intercept gives the saturation magnetization of the ordered phases. The intrinsic susceptibility for both crystals is the same, while the saturation magnetization for the

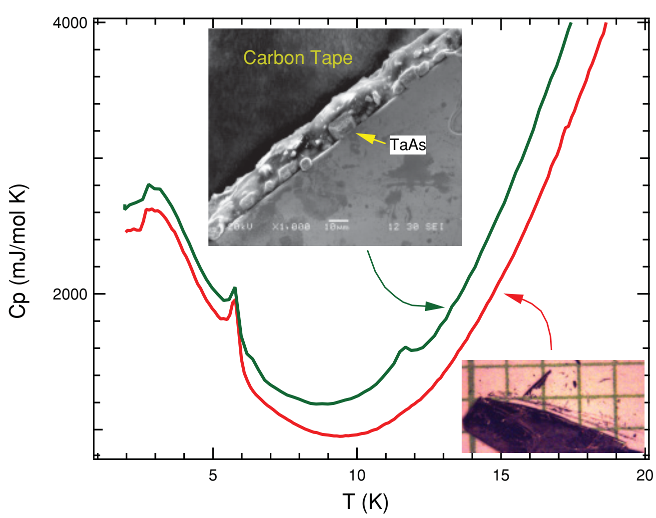

FIG. 4. (Color online) Temperature dependence of specific heat before and after mechanically removing the edges of NdFeAsO crystal no. 2. The upper inset shows a SEM picture of NdFeAsO single crystal no. 2 illustrating the residue on the crystal edge. The lower inset demonstrates how the residue on the edges was removed mechanically with a surgical blade.

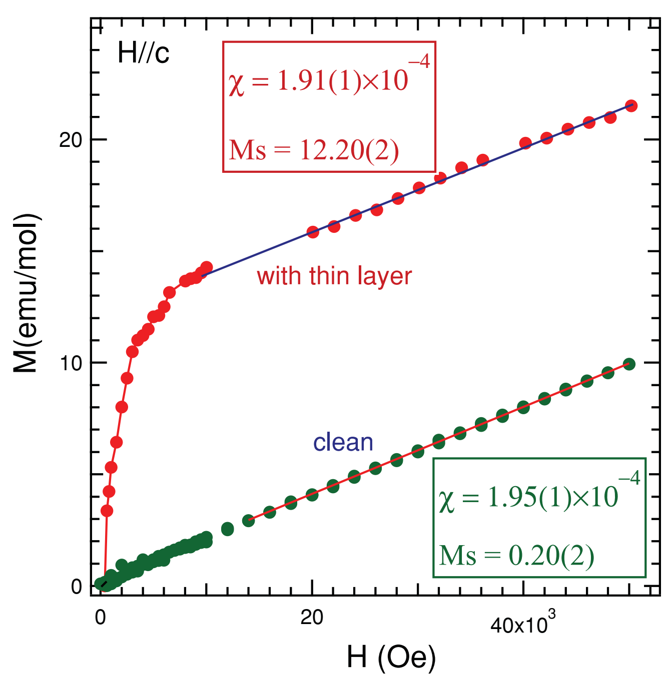

FIG. 5. (Color online) Magnetization M versus magnetic field H at 300 K with field parallel to the c axis for LaFeAsO crystals.

piece with the thin layer is about 60 times larger than that of the clean piece.

In summary, we studied the contribution of residual magnetic impurities to the magnetization of LaFeAsO and the specific heat of NdFeAsO crystals grown out of NaAs flux. Fortunately, the vast majority of these magnetic impurities are on the edges of the crystals and may be removed easily. Careful crystal selection and cleaning are suggested before measuring intrinsic physical properties.

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*jqyan@utk.edu. Present address: Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, USA; Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA.

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