Coaligning arrays of air-sensitive single crystals for inelastic neutron scattering experiments

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Abstract. The immense achievements of inelastic neutron scattering (INS) in recent years on the way to understanding the mechanism of high-temperature superconductivity were to a great extent enabled by the progress in fabricating large single-crystalline samples or coaligned mosaics consisting of up to several hundreds of individual single crystals. With the recent discovery of unconventional superconductivity in iron-based compounds, many of which can only be synthesized as relatively small crystals that rapidly decompose or deteriorate in air, we were faced with the technical challenge of preparing coaligned single-crystal arrays without exposing the samples to the ambient atmosphere. Here we describe a possible solution to this problem, which we have successfully employed to coalign both iron-pnictide and iron-chalcogenide single crystals in an argon atmosphere using a real-time digital x-ray Laue backscattering camera.

1. Introduction

For most of the high-temperature superconductors known today, including both copper oxides and iron-based compounds, high-quality single crystals can only be prepared in relatively small sizes, which are insufficient for inelastic neutron scattering (INS) measurements. Larger single crystals of both copper- and iron-based superconductors typically suffer from inclusions of foreign phases or doping inhomogeneities [1–3]. At the same time, the typical magnetic moments in these systems are small, of the order of one Bohr magneton or less. Therefore, to obtain reasonable intensity of the magnetic INS signal, sizable samples with a mass of several grams or more are desirable. To overcome this problem of sample size, INS measurements are often performed on large arrays of individual single crystals, coaligned on a sample plate (usually a thin aluminium grid or a silicon wafer) using x-ray Laue diffractometry [4–8]. Such crystal mosaics can include several tens or sometimes even more than a hundred [6, 8] of individual single crystals, mimicking a large single-domain crystal with a mosaicity determined by the accuracy of the coalignment. A typical mosaic spread of such arrays is of the order of 1–5°, defined as the full width at half maximum of the rocking curve measured across one of the structural Bragg peaks. Some of the largest cuprate samples prepared in this way for time-of-flight (TOF) spectroscopy measurements reached ~100 g in mass [9].

After the discovery of high-temperature superconductivity in iron-based compounds [10], this technique, which proved so successful for the copper oxides, also started to be applied to the new materials. Only for a few of the iron pnictides, such as electron-doped Ba(Fe1−xCo2x)2As2, whole large-sized single crystals with a mass exceeding 1 g could be synthesized [11, 12]. Most other compounds, in particular hole-doped Ba1−xKxFe2As2 [13] or pure KFe2As2 [14] that naturally...
grow in the form of small platelets, had to be coaligned into large arrays to reach the required sample size. One of the first such arrays prepared by our group is shown in Fig. 1. For some other families, most notably those with the ‘1111’-type crystal structure, even such a coalignment turned out to be impossible due to the tiny sizes of the so far available single crystals. As a result, INS experiments on the ‘1111’ family of iron pnictides until now remain limited to polycrystalline samples [15]. For a more complete overview of the INS results on iron pnictides, see Refs. 16–18.

2. Air sensitivity of iron-based superconductors

Different families of iron-based superconductors received disproportionate experimental attention, especially from INS, not only due to reasons related to the availability of sizeable single crystals, but also because of miscellaneous issues related to their chemical stability. As already mentioned, the ‘122’-type compounds have been investigated to a much greater extent than any other family, because these materials are typically stable in air and are easily available as large single crystals. However, even in these relatively stable compounds, changes in superconducting properties may occur after exposure of the samples to water vapor [19]. Other families of iron pnictides are more difficult to handle. For example, both Li$_{1-\delta}$FeAs and Na$_{1-\delta}$FeAs single crystals with the ‘111’-type structure, as well as their doped derivatives, are extremely sensitive to oxygen and air moisture [20,21,23] and decompose rapidly under ambient atmosphere. Therefore, meticulous care has to be taken to exclude any contact with air while handling the crystals over the entire process of sample preparation and measurements [24–26]. Some oxypnictides of the ‘1111’ family can also react with water vapor in air with the formation of a rare-earth hydroxide phase [27], though much less violently.

Undoped iron chalcogenides are known to be hygroscopic and can reportedly acquire superconducting properties after exposure to air within several days [28]. This could possibly result from an intercalation of water molecules or oxygen in between the crystallographic layers [29]. The recently discovered alkali-metal iron chalcogenide superconductors of the $A_xFe_{2-y}Se_2$ type ($A = K, Rb, Cs$) [30–32] are even more air-sensitive [32]. Their freshly cleaved surface typically degrades in air within several minutes [33] with a characteristic change of color, which seriously complicates the surface-sensitive Laue diffraction measurements. Bulk samples usually decompose on the scale of hours and therefore can only be exposed to air for very short times during sample mounting, which is by far insufficient for assembling multiple single crystals into a well-aligned mosaic.

Figure 1: One of our first coaligned arrays of platelike optimally doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ single crystals grown from Sn flux [34,35], assembled on a silicon wafer and mounted on an aluminium sample holder.
3. Airtight sample chamber for x-ray Laue measurements

To overcome this problem of air sensitivity, we have developed a simple and efficient way of manipulating air-sensitive samples during x-ray Laue backscattering measurements without exposing them to the ambient atmosphere. For this purpose, we have designed an airtight UFO-shaped chamber (see Fig. 2) that can be mounted vertically into the MWL 110 real-time digital Laue-backscattering system (Multiwire Laboratories, Ltd.), as shown in Fig. 3. To minimize the weight of the chamber, most of its components are made of aluminium. The top and bottom parts of the chamber form a standard ISO KF50-type flange and are connected together using a standard KF-type o-ring gasket and a lightweight chain clamp. On the side of the chamber facing the detector, there is a thin transparent window made of an elastic polymer film, such as the one used in membrane boxes for sample storage. The window is sufficiently transparent for the
Figure 4: The left panel shows an array of six Rb$_x$Fe$_{2-y}$Se$_2$ single crystals [36], coaligned on a silicon plate by means of the airtight sample chamber described in the text. The right panel presents a typical Laue diffraction pattern measured on one of these crystals.

x-ray beam, so that the Laue diffraction signal is visible on the detector. At the same time the elasticity of the film allows us to adjust the orientation of the samples inside the chamber directly through the membrane window without the need of opening the chamber at every iteration.

First, the sample plate is mounted inside the chamber as close as possible to the membrane window to allow enough space for sample mounting. If necessary, a spacer is placed below the sample plate to minimize the distance between the sample surface and the membrane window. Next, a single crystal is glued to the sample plate using a small amount of GE varnish inside a glove bag under a constant flow of argon. Immediately afterwards (before the varnish has time to harden), the chamber is closed and transferred to the Laue system, where the diffraction pattern from the sample is measured to estimate the misalignment of the crystal. Its orientation can then be adjusted immediately by pushing the crystal carefully through the membrane window with a soft ear-stick. Several iterations are usually required to reach an acceptably accurate orientation. After allowing some time for the varnish to solidify, the same procedure can be repeated for other single crystals until the complete mosaic is assembled. Finally, before the actual INS experiment, the assembled sample is removed from the chamber and mounted inside the cryostat in the usual way, without any extra foreign parts in the neutron beam.

Manipulating single crystals directly through the membrane without opening the chamber is a trick that allows us to save time and finish sample alignment before the varnish hardens, which would be much more difficult to achieve if the chamber had to be transferred to the glove bag and opened for every single adjustment of the crystal position. The elasticity of the membrane window also makes it possible to control the tightness of the chamber during measurements. A slight overpressure of argon is usually formed inside the chamber while the flange is being clamped, so that the membrane acquires a convex shape as can be seen in Fig. 3(a). The loss of this overpressure would indicate a leak, possibly due to a puncture in the membrane, which can be thus immediately noticed.

4. Results

We have successfully used the described method for characterizing and orienting individual single crystals of air-sensitive ‘111’-type iron pnictide materials [26] and for assembling several arrays of both K- and Rb-based ‘245’-type iron selenides (see Fig. 4) [36, 37]. The resulting samples consisted of up to 20 single crystals and were used both for TOF neutron spectroscopy [38] and for conventional triple-axis INS experiments [39, 40]. A typical Laue diffraction pattern from one of the Rb$_x$Fe$_{2-y}$Se$_2$ crystals is also depicted in Fig. 4. After the coalignment was completed, both K$_x$Fe$_{2-y}$Se$_2$ and Rb$_x$Fe$_{2-y}$Se$_2$ single crystals did not show any notable signs of surface degradation or any changes in their physical properties as compared to those constantly stored in argon atmosphere within a glove box.
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