Meissner and mesoscopic superconducting states in 1–4 unit-cell FeSe films

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We report a detailed investigation on the superconductivity in eight 1–4 unit-cell (UC) FeSe films on $SrTiO_3$ substrates by measuring their magnetization and sheet resistance in a field between 5×10^{-2} and 7×10^4 Oe over the last one and a half years as a function of temperature and frequency, from 2 to 300 K and from 0 to 1.5 kHz, respectively. The results show that samples of 1–4-UC FeSe films all display a complex superconducting structure, i.e., a Meissner state but populated with weak links below 20 K, and an unusual superconducting mesostructure up to 45 K, strongly suggesting that superconductivity may be of an interfacial nature. A model is proposed to account for the magnetizations in such a superconducting mesoscopic structure, similar to the Andreev reflection between the normal and superconducting carriers. Above 45 K, collective glasslike excitations are evident, although their nature is yet to be determined. The complex superconducting structure observed is consistent with the challenges in synthesizing ultrathin FeSe films with a superconducting temperature much higher than that of a bulk FeSe.

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I. INTRODUCTION

Recent reports [1–10] of interface-induced superconductivity in single-unit-cell (1-UC) films of FeSe on $SrTiO_3$ (STO) substrates with a high transition temperature T_c up to 100 K, in contrast to the ∼8.5 K of bulk FeSe [11], have generated great excitement. Such a high T_c is above the liquid nitrogen temperature and second only to that of the cuprate. Ultrathin FeSe films therefore exhibit the highest T_c among all Fe-based superconductors in spite of its having the simplest crystal structure. What makes it even more intriguing are the reports [1,3,9,10] that superconductivity appears only in the single-layer FeSe films but disappears when a second UC FeSe layer is added. In addition, the ultrathin films do not possess the hole pocket in the zone center for electron-hole nesting as in other layered high T_c superconductors. Apparently, it is also a challenge to synthesize these ultrathin FeSe films with a high T_c, as evidenced by the very small number of groups, mostly in China, that have produced the high T_c samples [12]. In spite of the great worldwide effort in the last two years, many questions remain. For instance, what is the nature of the superconducting state; what is the upper limit of T_c; does superconductivity occur only in the single-UC samples; and why are there so few successes producing samples with a high T_c?

Most of the high T_c's of ultrathin FeSe films reported to date were obtained from the energy gap opening temperature in tunneling or photoemission experiments. A possible contribution from energy gaps of a nonsuperconducting nature cannot be completely ruled out in these experiments. Crucial evidence for the existence of superconductivity at such high temperature in these ultrathin FeSe samples is yet to be established unambiguously, although a couple of rudimentary magnetic and resistive experiments [1,5–7] have been made. To address some of the questions posed above we have carried out a systematic investigation of the magnetic and resistive properties of ultrathin FeSe films.

Over the last one and a half years, we have measured the dc magnetic susceptibility in the zero-field-cooled mode (ZFC χ_{dc}) and field-cooled mode (FC χ_{dc}), the ac magnetic susceptibility ($\chi_{ac} = \chi'_{ac} + i\chi''_{ac}$), and the sheet resistance (R_s) of eight 1–4-UC FeSe films of different ages. Their values vary from sample to sample, not surprisingly, due to the delicate nature of these ultrathin film samples. However, the results show clear evidence of superconductivity—a strong Meissner state below 20 K—as shown by a field-effect diamagnetic shift of FC χ_{dc}. At the same time, a large diamagnetic χ'_{ac} with a strong component of logarithmic frequency dependence is also detected, suggesting the presence of weak links in the Meissner state. Although neither χ_{dc} nor χ'_{ac} at a frequency below $\sim 10^2$ Hz shows a noticeable diamagnetic drop above 20 K, χ'_{ac} above 10^3 Hz exhibits a diamagnetic shift with a distinct strong linear frequency-dependent component up to ∼45 K. This is attributed to a superconducting mesostructure based on a systematic examination on the aging, the phase angle $\theta = \arctan(\chi''_{ac}/\chi'_{ac})$, and the R_s of the samples. Above ∼45 K, a weak but distinct logarithmic frequency-dependent χ'_{ac} reappears, suggesting a glasslike excitation whose nature is yet to be determined. The complex superconducting structure detected in these ultrathin films of FeSe is consistent with the difficulty encountered in synthesizing these samples with a T_c higher than that for bulk FeSe.

It should be pointed out that we observed no systematic variation of the superconducting properties with the film thickness. For example, the χ'_{ac}'s at 2 K of our films, i.e., two 3-UC films, one 4-UC film, and one 1-UC film, are almost the same. This is in apparent conflict with the reports based on scanning tunneling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES) that superconductivity disappears with the presence of the second FeSe layer.

II. EXPERIMENT

The eight samples of dimensions 2 mm × 5 mm investigated consist of 1–4-UC FeSe layers deposited on STO substrates and capped by protective layers of Si/10-UC FeTe. They are all grown by the molecular beam epitaxy (MBE) technique by Q. K. Xue's group in Tsinghua University, Beijing, China. They are always sealed in quartz tubes in Ar except when being removed and measured. They were transferred to a plastic straw in a glove box for measurement in the Quantum Design Magnetic Property Measurement System (MPMS). Slow degradation is evident with samples aging continuously although slowly over a period of 18 months for the experiment. Their FC χ_{dc}, ZFC χ_{dc}, and $\chi_{ac} = \chi'_{ac} + i\chi''_{ac}$ have been measured in a field ($H = H_{dc} + H_{ac}$), where H_{dc} is the dc field from 0 to 5×10^4 Oe and H_{ac} the ac field from 0.1 to 3 Oe, and as a function of temperature from 2 to 300 K and frequency between 0 to 1.5 kHz, using the Quantum Design MPMS systems; and the ac four-lead R_s of two aged films at 17 Hz between 2 and 300 K in fields up to 7×10^4 Oe in the Quantum Design Physical Property Measurement System. The samples were positioned in a plastic straw with an incline angle $\theta°$ about 30° against the field H due to the sample dimension and the sample space constraints in the MPMS. Therefore the magnetic moment or the magnetic susceptibility measured consists of two components, one with H perpendicular to the sample and the other parallel to the sample. The extremely small thickness $d \sim 0.55$ nm and the small mass $\sim$(1–4) $\times$ 26 ng of the superconducting film give a magnetic susceptibility of $(1.3 \times 10^{-3})V_0\cos^2\theta_0(\frac{d}{\lambda})^2 \sim 4 \times 10^{-17}$ emu/Oe with parallel H where V_0 and λ are the FeAs volume and the penetration depth, respectively [13]. The value is too small to be detected with an estimated penetration depth $\lambda \sim 200$ nm. As a result, the magnetic data reported below are the magnetic susceptibility measured in an effective field $\sin\theta_0 H \approx 0.5\,H$ perpendicular to the film and amplified greatly by a large diamagnetic enhancement factor (see below).

III. DATA AND DISCUSSION

To improve the signal-to-noise ratio, repeated measurements were conducted to suppress the statistics fluctuations to below 10^{-8} emu/Oe. The background of the films was determined by measuring the χ'_{ac} of the film of Si/10-UC FeTe layers on the STO substrate (Fig. 1) to eliminate possible false signals of measurements. The background χ'_{ac} depends only slightly on temperature from 10 to 100 K but displays a weak jump below 10 K. The average values of χ'_{ac} and $d\chi'_{ac}/dT$ above 20 K as well as the χ'_{ac} jump below 20 K are -1.3×10^{-7} emu/Oe, -1.8×10^{-10} emu/(Oe K), and 1.6×10^{-7} emu/Oe, respectively. $d\chi'_{ac}/dT$ shows a very small downward shift around 70 K but R_s shows no sign of superconductivity down to 2 K. All χ'_{ac} results presented below have been corrected with the above background, which is assumed to be the same for all samples. It should be noted that all anomalies to be discussed are much greater than the background signal. We would like to point out that a significant dc ferromagnetic moment up to 10^{-4} emu may appear if proper demagnetization procedure is not followed. Such a signal can generate various artifacts in dc magnetic measurements of ultrathin films, especially in the presence of a strong measuring magnetic field. A proper demagnetization procedure has been followed in all our measurements, even though such a ferromagnetic background does not play a noticeable role in the ac susceptibility measurement, as assured by the absence of the thermomagnetic hysteresis.

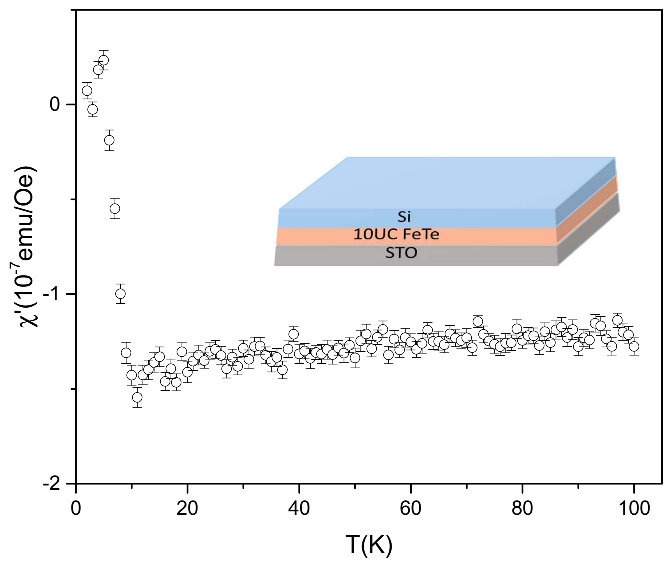

FIG. 1. (Color online) Ac magnetic susceptibility χ'_{ac} of the background of the sample (Si/10-UC FeTe/STO), at $H_{ac} = 1.5$ Oe and $\omega = 1488$ Hz. The error bars here and in Figs. 2–4, 7–12, and 14 represent the data spreads over 50 independent measurements. The inset represents the schematic structure for the Si/10-UC FeTe/STO.

A. Meissner state and superconducting volume fraction

The Meissner effect is considered to be a sufficient condition for the existence of superconductivity in a sample. It manifests itself by the expulsion of magnetic field from the sample when it is cooled to below T_c in the FC mode. The effect is indeed observed as a diamagnetic shift in FC χ_{dc} at 5 Oe as the sample is cooled below $\sim$20 K with $|\mathrm{FC}\,\chi_{dc}| \sim 3 \times 10^{-7}$ emu/Oe at 5 K together with a greater shift in $|\mathrm{ZFC}\,\chi_{dc}| \sim 10^{-6}$ emu/Oe, as exemplified in Fig. 2 for a 3-UC sample. The difference between $|\mathrm{ZFC}\,\chi_{dc}|$ and $|\mathrm{FC}\,\chi_{dc}|$ is attributed to the flux pinning associated with the

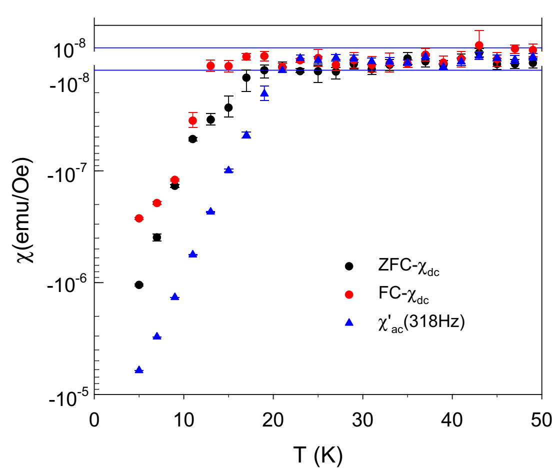

FIG. 2. (Color online) ZFC χ_{dc} and FC χ_{dc} at $H_{dc} = 5$ Oe, and χ'_{ac} at $H_{ac} = 1.5$ Oe and $H_{dc} = 0$ of a 3-UC FeSe film.

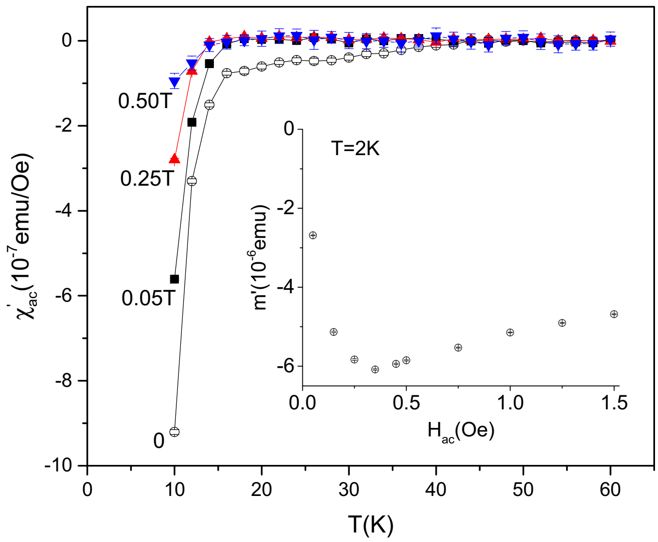

FIG. 3. (Color online) H_{dc} effect on χ'_{ac} at $H_{ac} = 1.5$ Oe and $\omega = 1488$ Hz for a 3-UC film. The inset represents m' vs H for $H_{ac} = 0$–1.5 Oe and $H_{dc} = 0$ at 2 K.

type II nature of the ultrathin FeSe films. Therefore, there is no question about the existence of superconductivity in ultrathin FeSe films, at least below ∼20 K.

In general, the superconducting volume fraction f should be between $4\pi|\mathrm{FC}\,\chi_{dc}|/V_0$ and $4\pi|\mathrm{ZFC}\,\chi_{dc}|/V_0$ if both the London penetration and demagnetization enhancement can be ignored. For the 3-UC film tested with an effective radius $r = 0.18$ cm and a thickness of $d \sim 1.65$ nm (i.e., a volume of $V_0 \sim 10^{-8}$ cm^3), the low-field $|\chi|$ is expected to be below $fV_0/4\pi \sim 10^{-9}$ emu/Oe without demagnetization enhancement, a value too small to be detected by our Quantum Design MPMS. The London penetration may further reduce the magnetization by a factor of $(\lambda/d)^2 > 10^4$ if the field applied is parallel to the film. The observed diamagnetic moments are mainly due to the demagnetization enhancement when $\theta_0 \neq 0$. Indeed, the $4\pi|\mathrm{FC}\,\chi_{dc}|/V_0$ and the $4\pi|\mathrm{ZFC}\,\chi_{dc}|/V_0$ at 5 K and 5 Oe correspond to $fA \sim 10^2$ and 10^3, respectively, where A is the effective demagnetization enhancement. The $4\pi|\chi'_{ac}|/V_0$ observed at 2 K, 318 Hz, and 1.5 Oe even reaches a $fA \sim 10^4$. While these values are still far lower than that for the low-field limit of an ideal superconductor with the same $r = 0.18$ cm and $d = 1.65$ nm, the expected edge field of $H_{ed} = H_{ac}(4r)/\pi d \sim 4 \times 10^6$ Oe should make vortex penetration unavoidable. The penetration will stop only when H_{ed} becomes lower than the lower-critical-field H_{c1}, i.e., after the penetrated vortices cut the film into smaller superconductive patches with effective radius $r' \sim H_{c1}\pi d/(4H_{ac})$. The upper limit of the A value will be $\sim 10^4$ with the applied $H_{ac} = 1.5$ Oe and the assumed $H_{c1} \sim 10^3$–10^4 Oe. Our data, therefore, suggest the majority of the film is covered by a superconductive layer. The interpretation is supported by both the 2 K $m'(\chi'_{ac}H_{ac}) - H$ data in Fig. 3 (inset) as well as the $R_s\,(T)$, which reaches zero at ∼10 K, suggesting that the two-dimensional (2D) percolation paths have been established.

The large diamagnetic superconducting signal of the 3-UC film is in disagreement with the previous STM-ARPES reports that the superconductive gap in the 1-UC film disappears after the second FeSe layer is added [1,3,9,10], although sporadic resistive studies also show superconductivity in a 5-UC film [1] and a 2-UC film [6], respectively. The present systematic resistive and magnetic study that has covered more samples with a number of layers up to 4 definitively shows the existence of superconductivity in all samples examined on a more solid ground. The observation of Meissner state and diamagnetic shift usually in ultrathin films indicates a rather large superconducting fraction of the samples and thus is difficult to reconcile with the negative STM-ARPES results, unless it takes place only at the interface as was previously suggested [1,8,14].

It should be pointed out that the thickness of the superconducting parts should not affect the magnetization observed. The expected $\chi'_{ac} \sim fAV_0/4\pi \propto \frac{r}{d}r^2 d$ is independent of the thickness d. Therefore, it is impossible to verify whether the superconductivity is limited to the single layer based on the magnetization results. However, the detection of superconductivity in the 1–4-UC samples shows that superconductivity cannot be suppressed by the second FeSe layer.

B. Diamagnetic shift in ac magnetic susceptibility up to 45 K

In line with the common expectation, we found that the 20 K $\chi'_{ac} \approx -1.3 \times 10^{-8}$ emu/Oe at low frequency; i.e., at 318 Hz, it is almost the same as the ZFC $\chi_{dc} \approx -0.7 \times 10^{-8}$ emu/Oe within a fluctuation of $\pm 4 \times 10^{-9}$ emu/Oe. It should be noted that the difference between the $|\mathrm{ZFC}\,\chi_{dc}|$ at $H_{dc} = 5$ Oe and the $|\chi'_{ac}|$ at $H_{ac} = 1.5$ Oe below 20 K are mainly the result of the nonlinear m-H discussed above (Fig. 3 inset). The associated ω dependence plays a rather minor role, as discussed later. Above 20 K the magnitude of the diamagnetic χ'_{ac}, however, appears to systematically increase with the measuring frequency ω. At 1488 Hz and $H_{ac} = 1.5$ Oe, for example, the χ'_{ac} is -6.2×10^{-8} emu/Oe, about 5 times higher than at 318 Hz. What is most unexpected is that this clear diamagnetic shift at $\omega = 1488$ Hz extends to a temperature up to ∼45 K as shown in Fig. 3 for the 3-UC FeSe sample. The temperature dependence $\chi'_{ac}(T)$ exhibits the standard responses to magnetic field for a superconductor, i.e., 0.05 T completely suppresses the diamagnetic χ'_{ac} above 20 K while the higher field continues to lower the diamagnetic χ'_{ac} below 20 K, but at a slower rate.

To further determine whether the diamagnetic shift below 45 K is associated with superconductivity, we have examined the χ'_{ac} and R_s of the samples as they aged. Both the magnitude of the diamagnetic χ'_{ac} and the associated T_c, i.e., the temperature below which diamagnetic shift occurs, are observed to decrease with aging as exemplified in Fig. 4. These are compared with the superconducting transition deduced from $R_s\,(T)$. The superconducting transition onset has been previously defined by the crossing point of the linear extrapolation line for the transition region and that above T_c [1,5]. To be consistent, a similar procedure was applied for two aged films. The T_c values so extracted, i.e., ∼30–35 K (Fig. 5), appear to be in line with the T_c extracted from the $\chi'_{ac}(T)$ for the same aged sample (red circles in Fig. 4) [15]. No dependence on the film thickness, i.e., 3 UC vs 4 UC, can be noticed. This strongly suggests that the diamagnetic shift at higher frequencies is caused by superconductivity.

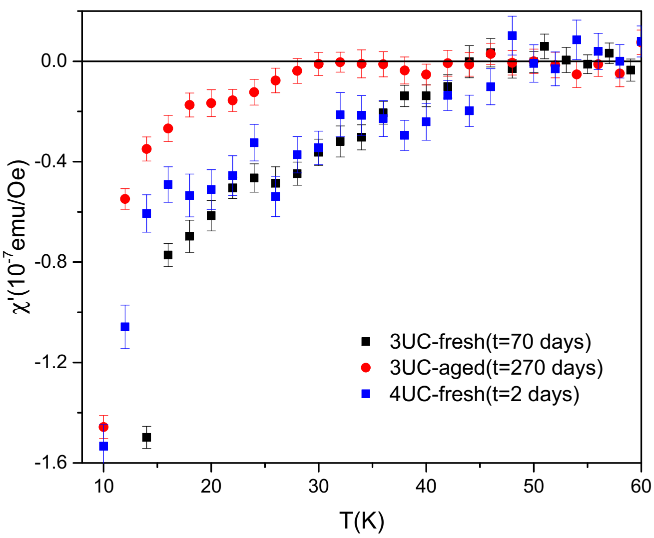

FIG. 4. (Color online) The χ'_{ac} at $\omega = 1488$ Hz for a 3-UC fresh film and an aged film, and a 4-UC fresh film.

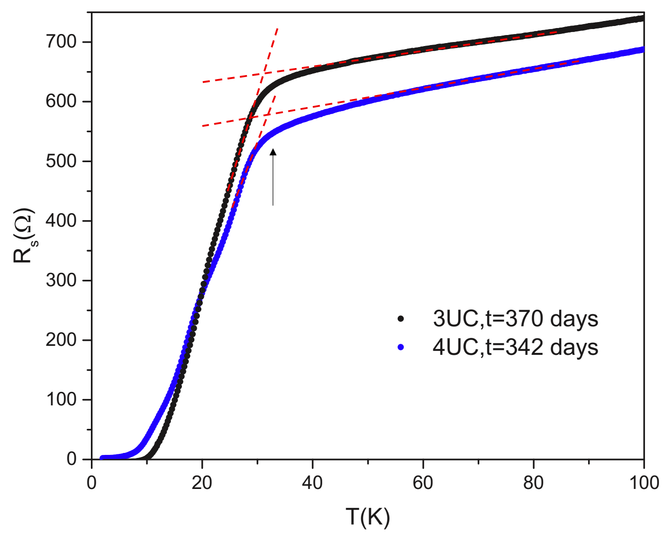

FIG. 5. (Color online) The sheet resistance R_s of an aged 3-UC film and an aged 4-UC film at $H = 0$. The red dashed lines are used for T_c extrapolation.

The diamagnetic shift $\chi'_{ac}(T)$ of the fresh film, therefore, demonstrates a T_c onset of 45 K or slightly higher if this is the case.

In the absence of the resistance data for fresh samples, we extract their resistively determined T_c by comparing their differently determined T_c's at different ages. We found that over a long period of 450 days, the magnetically and resistively determined T_c's degrade with time t as 48–0.06 t for the 3- and 4-UC films and the T_c of the fresh sample is $\sim$45 $\pm$ 3 K. It is also interesting to note that there are no systematic differences between the 3-UC film and the 4-UC film in terms of the aging (t) as shown in Fig. 6. Both the T_c onset and the 2 K χ'_{ac} are almost the same at a given t.

C. The different frequency responses of the ac magnetic susceptibility in different temperature regions

For a simply connected ideal bulk superconductor without flux penetration, both R_s and χ'_{ac} in the superconducting state are not affected by frequency (ω) until ω reaches the superconducting energy gap. The observed frequency dependence above 20 K presents a challenge. Several factors may cause differences between the dc and ac magnetizations, e.g., *p*-*n* junctions, flux dynamics, and the time scale involved. The linear m' vs H_{ac}, as well as the fact that the same ω dependence persists to very low field (i.e., $H_{dc} = 0$ and $H_{ac} = 0.05$ Oe), makes the first two possibilities less likely. We have therefore carried out a careful and systematic examination of the ω-effects on χ'_{ac} and χ''_{ac} of the ultrathin films of different ages at different temperatures and fields as a function of frequency in the range of 0–1.5 kHz, limited by the MPMS used. Several well characterized materials were also measured as references for comparison.

As mentioned earlier, the measured values of χ'_{ac}, χ''_{ac}, and χ_{dc} vary from sample to sample. However, we found that the magnitude of the diamagnetic χ'_{ac} continues to increase with ω above that of χ_{dc} below 45 K, and its ω dependence evolves from predominantly logarithmic to quasilinear and back to logarithmic as the temperature increases from 2 to 80 K. At a specific temperature, the ω dependence of the diamagnetic χ'_{ac}, $\Delta\chi'_{ac} \equiv \chi'_{ac}(\omega) - \chi'_{ac}$ (1.6 Hz), consists of a logarithmic term and a linear term, i.e., $\Delta\chi'_{ac} = \alpha \log\omega + \beta\omega = \Delta\chi'_{\log} + \Delta'_{\mathrm{lin}}$, with $\Delta\chi'_{\log} = \alpha\log\omega$ and $\Delta\chi'_{\mathrm{lin}} = \beta\omega$. It is interesting to note that only one term dominates in a specific temperature region for superconductive films. For example, $\Delta\chi'_{ac}$ is dominated by $\Delta\chi'_{\log}$ below $\sim$15 K, by $\Delta\chi'_{\mathrm{lin}}$ around 20 K, and by $\Delta\chi'_{\log}$ between $\sim$45 and 80 K, as shown in Figs. 7(a)–7(d). On the other hand, χ''_{ac} is always positive and increases linearly with ω, as shown in Figs. 8(a)–8(d). $\chi''_{ac}(\omega)$ in general is small except at very low temperature, e.g., at 2 K, presumably due to the movement of the densely packed fluxoids penetrated at low temperature into these ultrathin film samples loaded with weak links, as demonstrated below.

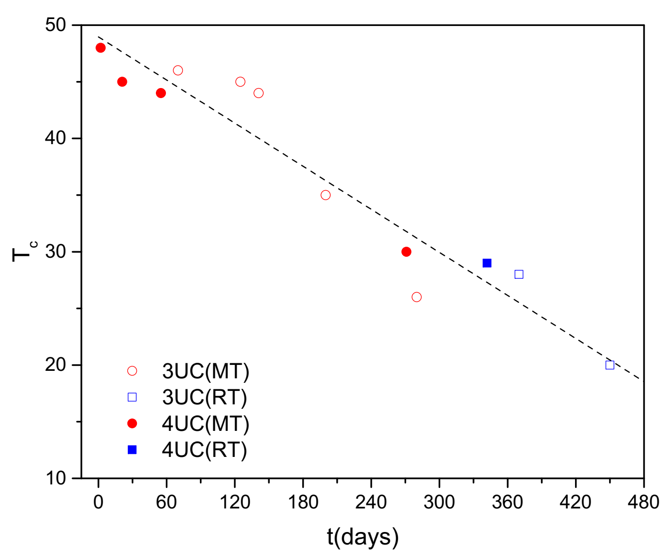

FIG. 6. (Color online) The aging of the resistive T_c onset (squares) and the magnetic T_c onset (circles) for a 3-UC film (open symbols) and a 4-UC film (solid symbols).

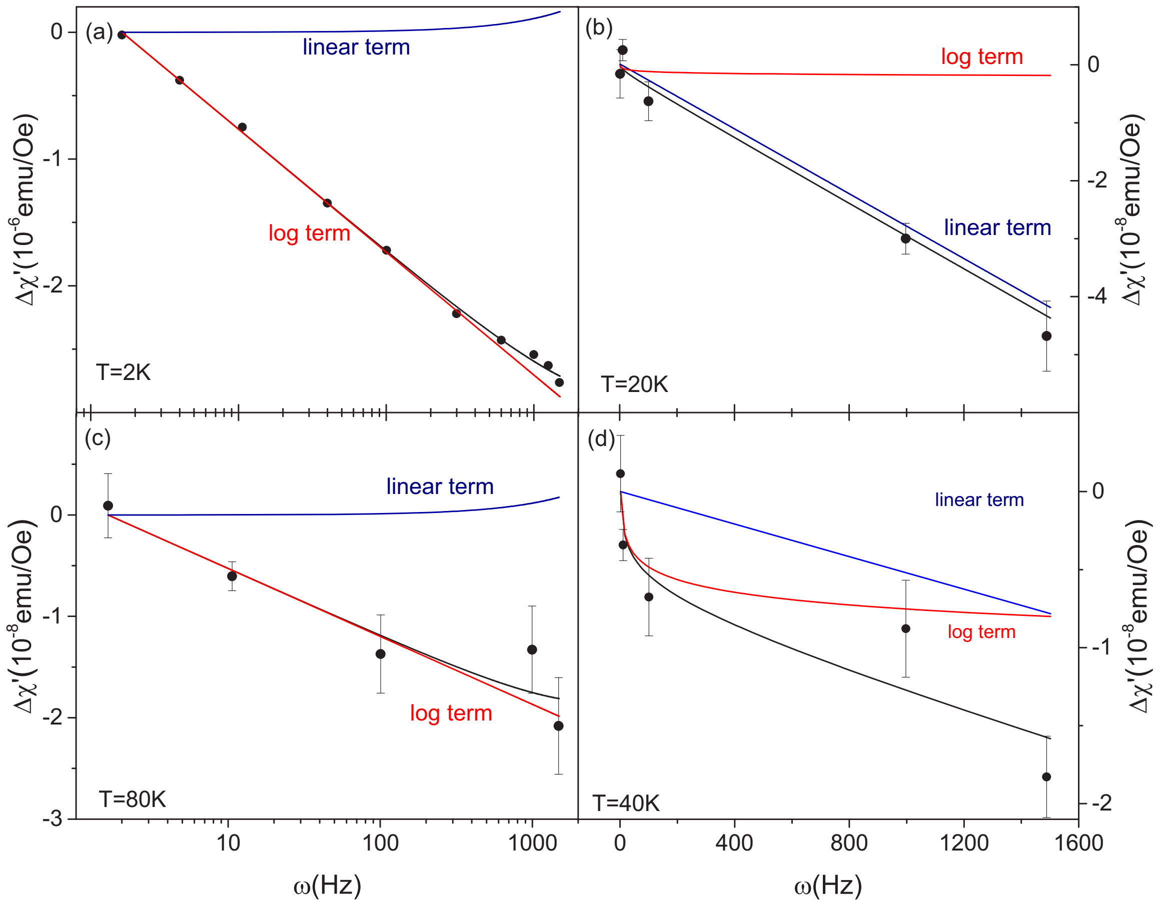

FIG. 7. (Color online) ω dependence of $\Delta\chi'_{ac}$ for a 3-UC film at different temperatures: (a) 2 K log scale; (b) 20 K linear scale; (c) 80 K log scale; and (d) 40 K linear scale. Black dots: raw data; black lines: $\Delta\chi'_{log} + \Delta\chi'_{lin}$; red lines: $\Delta\chi'_{log}$; blue lines: $\Delta\chi'_{lin}$.

1. The logω dependence of χ'_{ac} below 20 K

As shown in Fig. 7(a), the χ'_{ac} of the fresh films at 2 K is dominated by the logω-dependent term with a negligible linear-dependent term. This logarithmic ω dependence apparently exists continuously in the film after 1 year.

Similar logarithmic frequency dependence of the magnetic susceptibility has been observed previously in many other systems. For instance, it is well known that χ'_{ac} of a spin glass depends on frequency logarithmically over a broad frequency range [16]. This was initially attributed to a relaxation time spectrum [17]. The *ac* response is thus regarded as the superposition of many independent relaxation processes with different characteristic times τ. The τ is further associated with an energy barrier $\Delta \propto kT \ln \tau$. It has been shown that a logarithmic dispersion will naturally appear if Δ has a flat distribution. Later investigations reveal that such a Δ distribution is in fact the consequnce of the dynamic scaling of the renormalization theory: The length scale in a glassy system varies with time. All other parameters, such as Δ, should scale with the lengthscale, and the logarithmic dispersion follows naturally [18].

The glass states may not be limited to the spin system. Ebner and Stroud pointed out that the ac response of a weakly coupled disordered system of nanosuperconductors is very similar to that of spin glasses [19]. Similar logω, the response of the ac magnetic susceptibility, has indeed been observed in La_2CuO_{4-y} sintered polycrystalline samples under fields, which initiated the investigation of vortex glasses [20]. The ac response observed at 2 K [Fig. 7(a)] strongly suggests that the ultrathin FeSe films are in a superconducting glass state. The mesostructure and the associated weak superconductivity previously reported in FeSe films are consistent with this interpretation [21]. Therefore, even fresh films at low temperatures can be regarded as heterogeneous superconductors loaded with weak links created by possible complex cooling during synthesis of the samples.

2. The linear ω dependence of χ'_{ac} up to 45 K

As mentioned above, the ω dependence of the diamagnetic $\Delta\chi'_{ac}$ in general fits well by two terms, i.e., $\Delta\chi'_{ac} \equiv \chi'_{ac}(\omega) - \chi'_{ac}(1.6\,\text{Hz}) = \alpha\log\omega + \beta\omega$. Although the magnitude of χ'_{ac} decreases with increasing temperature, the relative strengths of the two terms vary with temperature nonmonotonically as exemplified in Figs. 7(a)–7(d). For instance, the logω term dominates at both 2 K and above 50 K, but the linear ω term prevails at 20 K. Actually, the $|\Delta\chi'_{log}|$ clearly drops rapidly with increasing temperature from 3×10^{-6} emu/Oe at 2 K to $\sim 5 \times 10^{-7}$ emu/Oe at 10 K, and becomes practically zero between 20 and 45 K [Fig. 9(a)] while the $\Delta\chi'_{lin}$ deviates from practically zero only in a limited range of 5–45 K and peaks to $\sim -7 \times 10^{-8}$ emu/Oe at 10 K [Fig. 9(b)].

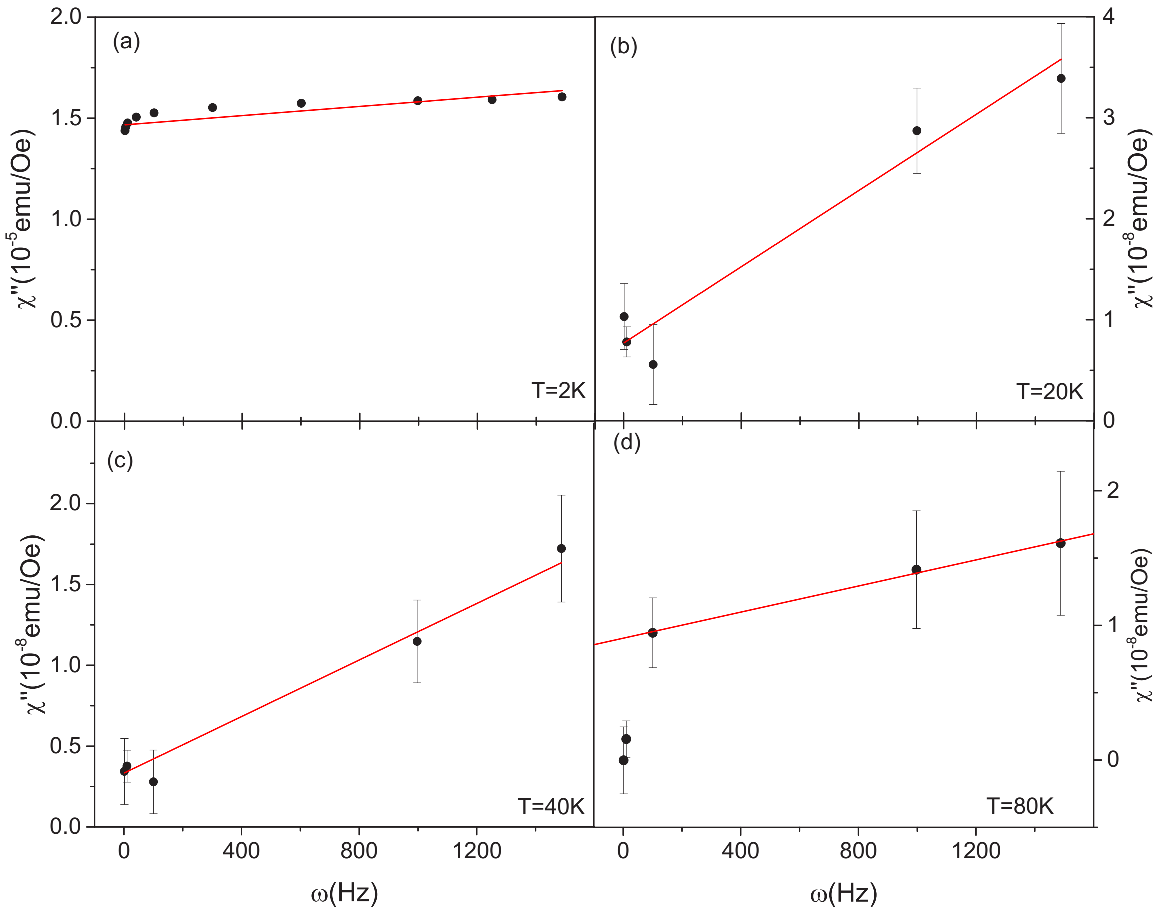

FIG. 8. (Color online) ω dependence of the χ'' for a 3-UC film at different temperatures. (a) 2 K; (b) 20 K; (c) 40 K; and (d) 80 K. Black dots: raw data; red lines: linear fitting.

The logω dependence of $\Delta\chi'_{ac}$ in the temperature region of 2–20 K can be understood in terms of a superconducting glass state due to the weak links present in the ultrathin superconducting FeSe films, as described earlier. The detection of a clear diamagnetic shift above 20 K only in χ'_{ac} at 1.5 kHz but not in either χ_{dc} or χ'_{ac} at 318 Hz (Figs. 2 and 3) strongly suggests that the shift is associated with the quasilinear component $\beta\omega$, and the persistent current loops are undetectable due to the small sizes of the weak-link-free superconductive cores. We have therefore investigated the field effects on their magnetic moments at different temperatures. The m'-H at 2 and 10 K clearly exhibits the characteristic behavior of a typical superconductor with flux penetration occurring far below ~0.1 Oe at 2 K, the lowest field tested (Fig. 3 inset). Similar behavior was also detected at 10 K but with flux penetration at smaller fields as expected. As the temperature increases to 20 and 30 K, the diamagnetic m' decreases as expected. But a completely unexpected field effect was detected at 20 and 30 K as shown in Fig. 10. The diamagnetic m' of these ultrathin FeSe films is observed to increase linearly with H up to 1.5 Oe, i.e., no evidence for flux penetration. The observation suggests that decoupled superconducting patches must exist in these samples at these high temperatures. These superconducting patches could be of the same material that is superconducting throughout the film but become decoupled above 20 K, or of a different material with a T_c above 20 K and uncoupled already below 20 K. If the latter is true, the observation could have a profound implication in the future search for superconductors of higher T_c.

3. *Aging of 2 K superconductivity*

To further explore the root of such unusual pseudolinear dispersion, the aging of $\chi'_{ac}(\omega)$ at 2 K was systematically investigated. As discussed above, the films are in a superconductive glass state even at 2 K, and both the $\Delta\chi'_{log}$ and the χ'_0 (or χ'_{ac} at 1.6 Hz) represent the shielding provided by the supercurrents. It is interesting to note that both are degrading with aging time (t) in similar ways. The agreement was observed for two films for which we have kept records. Some of the superconducting parts, especially those associated with the weak links, are expected to gradually convert into nonsuperconductors. Aging will therefore be expected to decouple large superconducting domains into decoupled patches. The data seem to support the above conjecture if decoupled patches are associated with the unusual quasilinear dispersions. For both films, their $\Delta\chi'_{lin}$ at 2 K initially shifts abnormally from almost zero to negative with increase of t. For example, the $\Delta\chi'_{lin}$ of a 4-UC sample evolves with time from $+4 \times 10^{-9}$ emu/Oe, i.e., magnetismlike at $t = 10$ days and to -2.5×10^{-8} emu/Oe and -4×10^{-8} emu/Oe after 270 and 350 days, respectively [Fig. 11(a)]. To further show this is neither accidental nor

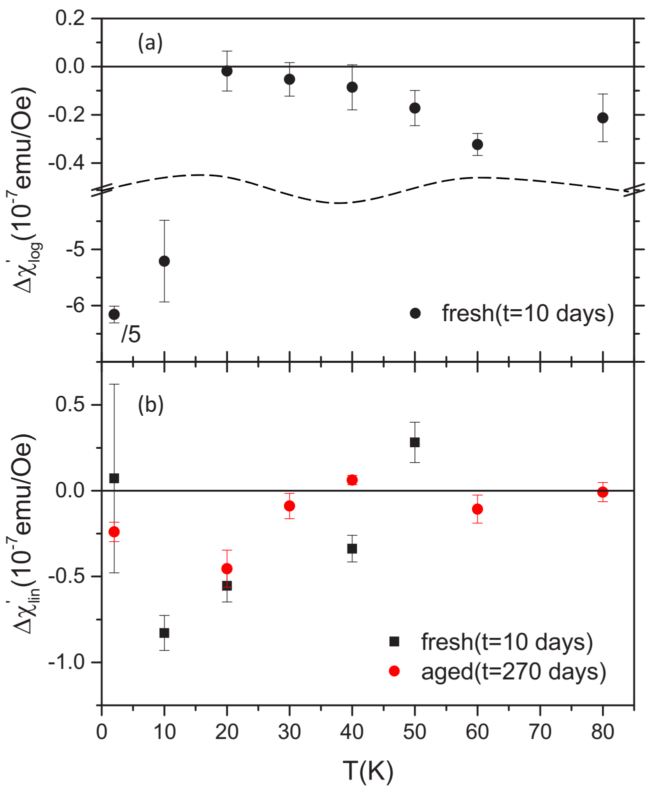

FIG. 9. (Color online) (a) $\Delta\chi'_{\rm log}$ vs T. The data at 2 K are reduced by a factor of 5 to fit the scale. (b) $\Delta\chi'_{\rm lin}$ vs T at $\omega = 1488$ Hz for a 4-UC film.

a fitting artifact, the raw isothermal $\Delta\chi'_{\rm ac}$ vs ω data of a 4-UC film at $t = 10$ and 350 days are shown in Fig. 12. A clear downturn appears above 10^2 Hz for the aged film (i.e., a negative linear term), but only a very minor upturn can be noticed in the fresh state. Further aging, however, suppresses this diamagnetic shift instead. While such suppression is only marginal at 2 K, i.e., after 360 days in Fig. 11(a), it is much

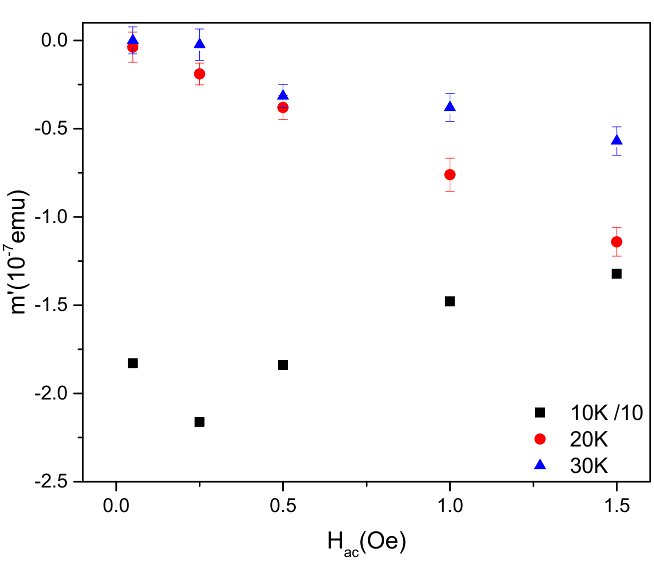

FIG. 10. (Color online) m' vs $H_{\rm ac}$ at 1488 Hz and $H_{\rm dc} = 0$ for a 3-UC film at different temperatures. The data at 10 K are reduced by a factor of 10 to fit the scale.

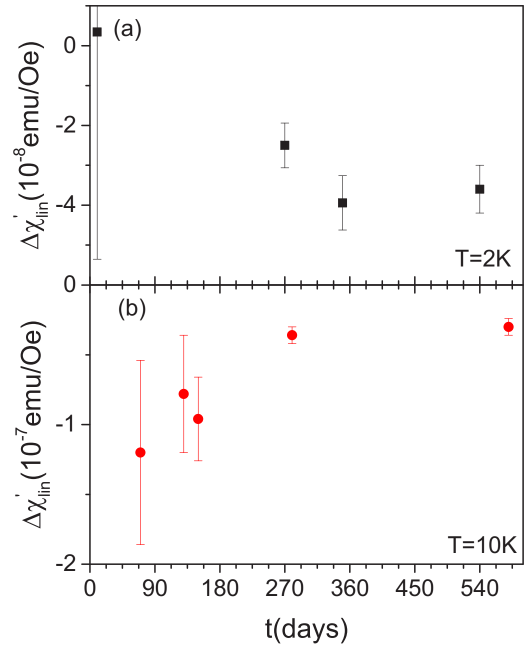

FIG. 11. (Color online) Evolution of $\Delta\chi'_{\rm lin}$ with time for a 4-UC film at different temperatures.

stronger at 10 K, where the coupling is weaker [Fig. 11(b)]. These suggest that the unusual initial enhancement of the 2 K $\Delta\chi'_{\rm lin}$ is better interpreted as the intermediate product of the degrading of the weak links: Coupled weak links (appearing as the logarithmic term of the superconducting glasses) first degrade into marginally decoupled junctions, i.e., coupling only with the help of normal carriers, before being totally destroyed.

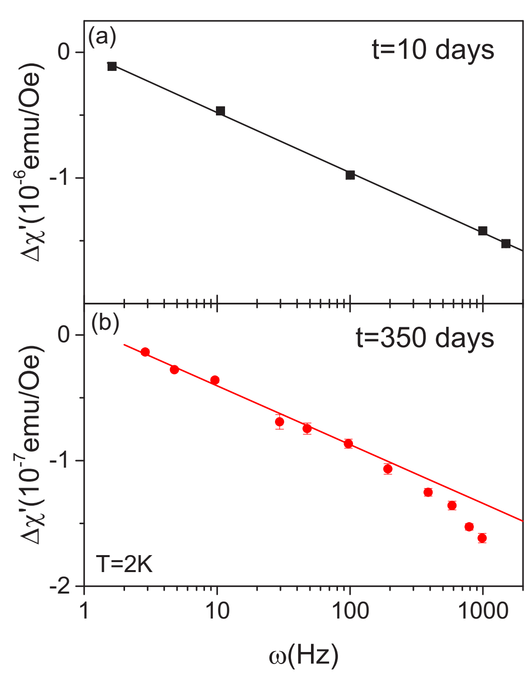

FIG. 12. (Color online) The $\Delta\chi'_{log}$ vs ω at 2 K for a 4-UC film of different ages.

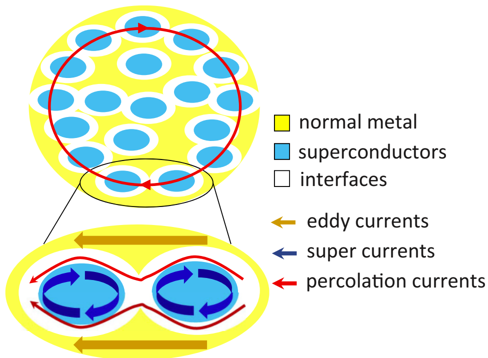

FIG. 13. (Color online) The proposed model for the quasilinear component in the observed ac response in FeSe films.

The detailed process involved in sample aging is still unclear. It may be related to minute moisture and/or oxygen pickups during the long period of even careful experimentation. In fact, we did find that complete exposure to Houston's humid air significantly destroyed the superconductivity of one of our samples in 0.5 h.

4. A provisional model for the unusual $\chi'_{ac}(\omega,T)$ observed

Currently, there exists no theory to describe the unusual frequency dispersion observed in the ultrathin FeSe films. A provisional model is therefore proposed as displayed in Fig. 13 for the samples with separated superconductive patches as described earlier.

Below the percolate threshold, percolate paths of supercurrent I_{sc} do not exist across a macroscopic length, i.e., the adjacent superconductive patches are typically separated by nonsuperconductive barriers with thickness much larger than the corresponding coherence length. The traditional superconducting screening is limited to within individual patches. The moment of a current loop is the product of the circulating current and the area enclosed. For small patches, the moments can be well below the noise level. The absence of a dc diamagnetic drop above 20 K suggests this is the case, i.e., the effective patch diameters are smaller than 1 μm. On the other hand, the normal eddy currents I_{ed} may cover the whole area. The associated moment may still be below the noise floor due to both the high R_s of the film and the 90° phase angle of the eddy currents, i.e., $\chi'_{ac} \approx 0$ [22]. The situation, however, may change when the superconducting patches are close enough to be within the mean free path of the normal carriers but still farther apart than the superconducting coherence length. The superconducting current I_{sc} within a patch and the surrounding normal I_{ed} are separated only by the interface. The momentum exchange between these two is inevitable, as demonstrated in the case of Andreev reflection. The momentum gained by the normal carriers at the surface of one patch may still be partially kept when they arrive at the adjacent patch. Percolation loops may be formed for such mixed carriers. While no phase coherence exists, the normal carriers and the supercarriers along a given loop contribute to the ac component of the momentum (or an ac current). While the I_{sc} is in phase with H_{ac} and contributes a χ'_{ac} independent of ω, the accompanying I_{ed} is out of phase with a χ'_{ac} proportional to ω^2. Momentum exchanges should mix both and a phase angle between 90° and 180° is expected. The resulting ω dependence of χ'_{ac} should also be somewhere between ω^0 and ω^2. The carriers with the modified phase angle and ω dependence may travel a distance far longer than that allowed across the Josephson junctions. Therefore, the net circulating current of I_{sc} and I_{ed} or the associated moment m' may display an ac phase angle θ between 90° and 180°, i.e., permit a noticeable χ'_{ac} even in the audio frequency band. The enhanced conductivity through the superconductive patches also helps.

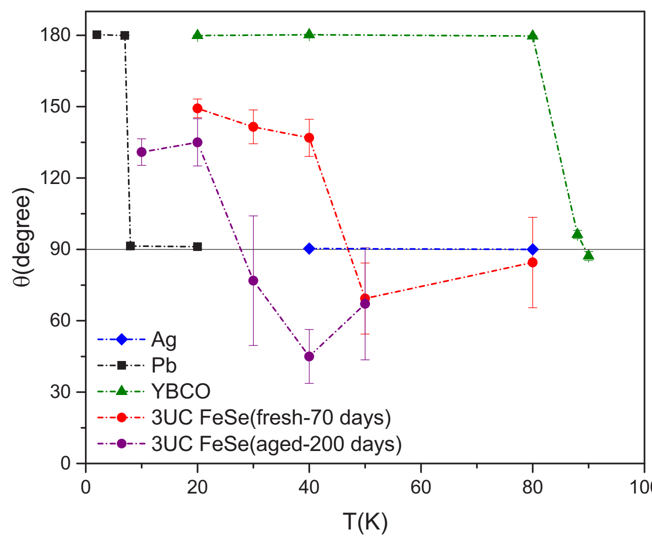

FIG. 14. (Color online) The ac phase angles of the moment of a Ag disk, a Pb sheet, an YBCO film, a 3-UC fresh film, and an aged film.

One way to experimentally elucidate the model is to examine the ac phase angle θ associated with the percolate current or m' with known superconducting and nonsuperconducting metals. The phase angles of three reference samples, a Ag disk, a Pb sheet, and an $YBa_2Cu_3O_7$ (YBCO) film, were measured at 1488 Hz as a function of temperature. As expected, $\theta = 90°$ for a normal metal is observed in Ag at all temperatures examined, in Pb above its T_c of 7.2 K, and in YBCO above its $T_c \sim 90$ K, and a $\theta = 180°$ is detected in Pb and YBCO below their T_c's as shown in Fig. 14. As for the ultrathin FeSe-film samples, θ of a fresh sample lies between 130° and 150° up to ~45 K and becomes below 90° above 45 K; while that of an aged sample is about 130° below ~30 K but drops to below 90° rapidly at higher temperatures. The observation is consistent with the suggestion that superconductivity exists up to ~45 K in the fresh ultrathin FeSe-film sample and up to ~30 K in an aged sample. While the existence of a minor superconducting phase cannot be decisively excluded, both the phase angle and the logarithmic ω dependence suggest that the glasslike spin excitations are the likely dominant causes above 45 K [23].

IV. CONCLUSION

The magnetization and resistivity of several FeSe films have been measured. Independent of the number of FeSe layers, both Meissner effect and superconductive glass behaviors have been observed below 20 K. Above 20 K the diamagnetic susceptibility up to 45 K becomes noticeable only in the ac susceptibility at $\omega > 10^3$ Hz, indicative of possible interface-enhanced superconductivity in these ultrathin FeSe films. An unusual quasilinear ac frequency dependence as well as the associated aging effect demonstrate that all of these are rooted in superconductivity. We propose a model to relate such an ac response to a mesostructure of separated superconductive nanopatches.

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