Resonant ultrasonic spectroscopy and resonant piezoelectric spectroscopy in ferroelastic lead phosphate, Pb$_3$(PO$_4$)$_2$

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Abstract

Elastic properties of the ferroelastic compound Pb$_3$(PO$_4$)$_2$ were investigated using resonant ultrasonic spectroscopy. Results show softening of the mechanical resonance frequencies at the $R3m$ $\rightarrow$ $C2/c$ ferroelastic transition temperature $T_{\text{trans}}$ = 453.6 K with no noticeable frequency dispersion. The reduction of resonance frequencies corresponds to 25% softening of the effective elastic constants at $T_{\text{trans}}$ relative to the value at 700 K. The data analysis indicates that the elastic precursor softening is driven by a displacive soft mode that is coupled to the order–disorder movements of Pb atoms around the rhombohedral threefold axis, which gives rise to local monoclinicity in the paraelastic phase. Finally, resonant piezoelectric spectroscopy (RPS) is used to determine if microstructures are polar in the cubic phase. RPS measurements find no evidence of piezoelectric signals in Pb$_3$(PO$_4$)$_2$, confirming that the possible polar behavior detected using second harmonic generation is due to crystal imperfections.

(Some figures may appear in colour only in the online journal)

1. Introduction

Lead phosphate, Pb$_3$(PO$_4$)$_2$, was the first ferroelastic material where a full ferroelastic hysteresis was measured [1] and has become a model compound for ferroelastic distortions. The phase transition is first order and occurs at $T_{\text{trans}}$ = 453.6 K [2–8], leading to a structural change from trigonal (space group $R3m$) to monoclinic symmetry (space group $C2/c$). This structural change is provoked by the off-centering of Pb ions from the triad axis and subsequent lattice relaxation, including tilting of the PO$_4$ tetrahedra [4, 7]. In the (monoclinic) ferroelastic phase, the off-centering of Pb ions gives rise to high densities of twin boundaries which are pinned at low temperature but are mobile at temperatures near $T_{\text{trans}}$ [4, 9, 10]. The off-centering of Pb ions is also evident above $T_{\text{trans}}$, which leads to a microstructure of locally monoclinic (ferroelastic) domains in the rhombohedral (paraelastic) matrix [4, 7–9]. Although recent x-ray measurements indicate the existence of monoclinic microstructures up to 468 K [8], earlier studies have found that monoclinic microstructures exist up to a temperature between 530 and 563 K [4, 6, 7, 10, 11]. In addition, a theoretical study has indicated that they should be dynamic [9]. This has been confirmed by Raman scattering measurements, with the observation of a so-called flip mode in the paraelastic phase [10]. The flip mode has an estimated frequency of $\sim$10$^{10}$ Hz and arises from spontaneous thermal switching between the three binary axes of the monoclinic structure which are symmetry equivalent in the trigonal phase. The flip mode is believed to continue to operate also below the transition point, giving reorientational motion of microdomains within macroscopically monoclinic twin domains between $T_{\text{trans}}$ and $\sim$430 K [4, 7, 10, 12, 13].

According to dynamic mechanical analysis measurements at $\sim$1 Hz, the elastic moduli of Pb$_3$(PO$_4$)$_2$ soften by up to 80% with falling temperature through the transition. This softening starts at $\sim$700 K but occurs mainly in vicinity of $T_{\text{trans}}$ [2], and is due to a combination of the dynamic microstructures and strain relaxations coupled to the displacive soft mode. On the other hand, Brillouin scattering, which probes elastic properties at frequencies in the GHz range, has shown only 30% softening in the elastic
constant $C_{66}$ as the transition point is approached from above, followed by a small degree of stiffening immediately below the transition point, with even smaller changes in the other elastic constants [14]. The difference indicates that the contribution of the intrinsic part (soft mode and flip mode) to the softening is small in comparison with that of the extrinsic part (twins walls and two phase interfaces). Furthermore, the relaxation time for the mobility of interfaces in the transformation microstructures is likely to be somewhere between the two extremes of the measuring techniques. These elastic properties are clearly revealing of both the nature of the ferroelastic phase transition and the microstructures which are related to it. The first objective of the present study, therefore, was to place tighter constraints on the dynamic properties of the transformation microstructures by measuring the elastic and anelastic properties of single crystals at frequencies of $\sim$0.1–1 MHz using resonant ultrasound spectroscopy (RUS) between room temperature and 1060 K.

Although the favored space group for the low-temperature space group is $C2/c$ [4, 7, 8], Kiat et al [15] reported it as being $C2$, which is noncentrosymmetric and allows a spontaneous polarization. They supported this claim with second harmonic generation (SHG) spectroscopy. On the other hand, the observation of the SHG signal both below and above $T_{\text{trans}}$ by Bieser et al [16] was attributed to oxygen defects. Whether the SHG signal is due to intrinsic characteristics of $\text{Pb}_3(\text{PO}_4)_2$ or oxygen defects is still unresolved, and the second objective of the present study was to apply a new experimental method, resonant piezoelectric spectroscopy (RPS) to both the paraelastic and ferroelastic phases in order to test for the presence of piezoelectric domains. RPS measurements provide a straightforward method for detecting local or macroscopic regions of a crystal which are piezoelectric [17, 18].

### 2. Methods

The $\text{Pb}_3(\text{PO}_4)_2$ samples were cut from a single crystal grown using the Czochralski technique [7]. The dimensions of sample 1 were $\sim$2 mm $\times$ $\sim$0.5 mm $\times$ $\sim$4 mm, with the longest dimension pointing along the [100] direction. Sample 2 had roughly the shape of a parallelepiped with dimensions of $\sim$2.5 mm $\times$ $\sim$2.8 mm $\times$ $\sim$3.1 mm. RUS measurements [19, 20] were performed using a Netzsch 1600°C furnace, as described elsewhere [21]. Sample 1 was mounted across the smallest parallel faces between the tips of the alumina rods, which extend into the furnace, while sample 2 was mounted across its corners. For RUS an AC voltage of 10 V was applied across the emitter transducer, located in the end of the alumina rods outside the furnace, and the second transducer at the end of the other rod acted as the detector. RUS data from sample 1 were collected up to 1060 K in heating sequences with temperature steps as shown in table 1. For sample 2, data were collected on heating in 10 K steps between 290 and 420 K and in 1 K steps between 420 and 478 K. Individual spectra were collected after a settle time for thermal equilibration of 20 min at each temperature. The spectra contained 50,000 data points between 0.1 kHz and 1.2 MHz and were analyzed using the software package IGOR PRO (WaveMetrics). The frequencies of the sharpest mechanical resonance peaks and their widths at half height were determined using an asymmetric Lorentzian fit function.

Table 1. Heating sequences and corresponding temperature steps used for RUS measurements on $\text{Pb}_3(\text{PO}_4)_2$ (sample 1) between 293 and 1059 K.

| Heating sequences | Steps (K) |
|-------------------|-----------|
| 293–413           | 10        |
| 413–433           | 5         |
| 433–487           | 1         |
| 487–487           | 3         |
| 539–619           | 5         |
| 619–1059          | 20        |

The experimental arrangement for RPS has been described in detail elsewhere [17, 18] and is based on the excitation of elastic waves by applying an AC voltage of 1–25 V directly across the sample rather than the emitter transducer. If the material has locally or macroscopically broken inversion symmetry, the driving voltage leads to the excitation of local distortions that lead to macroscopic resonant elastic waves. The resulting elastic resonance is observed using the detector transducer as for RUS. RPS has been successfully tested in the ferroelectric materials and relaxor ferroelectrics, such as BaTiO$_3$, in which there is evidence of polar nanostructures in its paraelectric phase [17]. The largest parallel faces of sample 1 were covered with silver paint, and an AC voltage of 20 V was applied using copper wires attached to the layer of silver paste on the sample surfaces. Spectra were collected between 400 and 550 K in 20 K steps over a frequency range from 100 to 1.2 MHz. The equilibration time at each temperature was 15 min.

Using both methods mechanical resonance peaks associated with both the sample as well as the alumina rods are detected, but the latter can be identified quite easily since they show little or no dependence of frequency on temperature.

### 3. Results

Segments of some RUS spectra from sample 1 collected between 290 and 900 K are shown in figure 1. They are offset in proportion to the temperature at which they are collected and the $y$ axis is labeled as temperature. Temperatures were scaled according to the known $R3\bar{m} \rightarrow C2/c$ transition in $\text{Pb}_3(\text{PO}_4)_2$ by choosing the temperature at which the resonance frequencies of individual peaks was lowest as being $T_{\text{trans}} = 453.6$ K [4, 6, 8]. This spectrum is displayed in blue. Note that peaks which do not show any overt temperature dependence are from resonances of the alumina buffer rods. For temperatures above 860 K, a gradual increase in the amplitudes of resonance modes was accompanied by an increase in the rate of change of frequency upon heating (not shown). These observed variations in the peak amplitudes and frequencies are attributed to the chemical decomposition of $\text{Pb}_3(\text{PO}_4)_2$.

While sample peaks are clearly visible in figure 1 for temperatures above $T_{\text{trans}}$, only a few of them with
weak amplitudes exist in the monoclinic phase and they disappear below $\sim 430$ K. In order to determine whether the overdamping of sample resonances below $T_{\text{trans}}$ is reproducible, a set of experiments was performed using sample 2. Segments of spectra obtained from this sample are presented in figure 2, where the spectrum shown as a blue line was again assumed to be that for $T = T_{\text{trans}}$. For clarity, let us point out that the resonance labeled as $\omega_2$ belongs to sample 2 whereas the resonances labeled as $\omega_1$ and $\omega_3$ in the following paragraphs belong to sample 1. As shown in figure 2, $\omega_2$ ranges between 235 and 275 kHz, with a minimum assumed to be at $T_{\text{trans}}$. Unlike the resonance modes of sample 1 below $T_{\text{trans}}$ (figure 1), the resonance mode $\omega_2$ shown in figure 2 experiences no significant damping down to 430 K.

The temperature dependences of the squared frequencies $\omega_1^2$ and $\omega_2^2$ are presented in figure 3(a). The square of a resonance frequency is proportional to the effective elastic modulus $C_{\text{eff}}$ associated with that mode. The effective modulus $C_{\text{eff}}$ is typically some combination of compressive and shear elastic constants while the lowest frequency modes usually depend on the softest combination of shear elastic constants. As shown in figure 3(a), with decreasing temperature the frequency of $\omega_2^2$ decreases down to the ferroelastic transition temperature $T_{\text{trans}}$. This decrease corresponds to a $\sim 25\%$ reduction of the effective elastic constant at a temperature just above $T_{\text{trans}}$ relative to the value at $\sim 700$ K. For comparison with Brillouin scattering measurements, the relative variations of $\omega_1^2$ and $\omega_2^2$ are combined, as described in the caption of figure 3, and replotted in figure 3(b) alongside $C_{66}$, which is taken from figure 2 of Torres et al [14]. Remarkably close agreement at $T > T_{\text{trans}}$ implies that the RUS data may also refer predominantly to $C_{66}(=0.5(C_{11} - C_{12}))$, which is the softest shear elastic constant according to the Brillouin scattering measurements [14]. For comparison with DMA data, the variation of the elastic modulus from figure 2 of Harrison et al [2], scaled in the same way, is shown as a green continuous line in figure 3(b). Again, there is close agreement with the other data at $T > T_{\text{trans}}$, suggesting an absence of, or only very weak dispersion with frequency in the stability field of the parent rhombohedral structure.

While there might be good agreement between DMA, RUS and Brillouin scattering data, probably for $C_{66}$, at $T > T_{\text{trans}}$, there are larger differences between the elastic behavior measured at $T < T_{\text{trans}}$. There are still some differences between the RUS and Brillouin data but the form is similar and clearly very different from the DMA result. The superelastic softening below $T_{\text{trans}}$ seen by DMA is known to be related to the back and fore motion of needle twins [2]. These are presumably not occurring under the frequency and stress conditions of an RUS experiment, which is more nearly measuring the intrinsic softening seen by Brillouin scattering.

Figure 4 shows the inverse mechanical quality factor, $Q^{-1}$, for resonances $\omega_1$ (number symbols), $\omega_2$ (plus signs, see figure 2), and $\omega_3$ (stars). The resonance $\omega_3$ ranges between 225 and 270 kHz in the temperature interval $T_{\text{trans}}$ to 700 K. With decreasing temperature, $Q^{-1}$ from the $\omega_2$ peak shows negligible variation down to $T_{\text{trans}}$. As the ferroelastic transition temperature is approached, a slight increase in
Figure 3. Temperature evolution of (a) the resonant frequencies $\omega_1^2$ (of sample 1) and $\omega_2^2$ (of sample 2) of Pb$_3$(PO$_4$)$_2$. (a) The squared frequencies of the mechanical resonance mode of sample 1 located around $\omega_1 \sim 200$ kHz (blue circles) and that of sample 2 located around $\omega_2 \sim 200$ kHz (black squares). (b) Comparison of $\omega_1^2$ and $\omega_2^2$ with the elastic constant $C_{66}$ of Pb$_3$(PO$_4$)$_2$ from [14] and the elastic modulus obtained with DMA [2]. Data for $\omega_1^2$ and $\omega_2^2$ were normalized relative to their values at 700 K and 476 K, respectively, and the relative variation of $\omega_2^2$ was vertically translated to match the softening of $\omega_1^2$ at 476 K.

Figure 4. Temperature evolution of $Q^{-1}$ from RUS measurements in comparison with tan $\delta$ determined using DMA [2]. The modes $\omega_1$ (number symbols) and $\omega_3$ (stars) belong to sample 1 and $\omega_2$ (plus signs) is a resonance of sample 2. The RUS data are also shown in the inset figure for clarity. Note that an instrumental background has been removed from the DMA so that they overlap with $Q^{-1}$ data at $T > T_{trans}$. Labels $P_i$ indicate the peak points of mechanical attenuation.

According to Harrison et al [2], peak $P_1$ in the DMA data is due to displacements under applied stress of interfaces between locally rhombohedral and locally monoclinic domains within the crystal, $P_2$ marks a crossover from this to motion of twin walls as the dominant loss mechanism, $P_3$ appears to be associated with freezing out of local flip disorder within the ferroelastic domains and below $P_4$, which is located at $\sim 400$ K and not shown in figure 4, the motion of needle twins becomes partially saturated. The peak in $Q^{-1}$ clearly corresponds closely with $P_1$ and is therefore attributed also to motion of the interfaces between coexisting rhombohedral and monoclinic structures. The absence of high loss below this peak implies that the movement of macroscopic twin interfaces does not occur as part of the mechanical resonances stimulated under RUS conditions. This is in contradiction to the observation for sample 1, however. Resonances of sample 1 experience strong damping below $T_{trans}$, which indicates that twin interfaces become mobile at RUS frequencies. The different behavior
of damping mechanisms in the two samples can be attributed to the orientation of twin walls relative to the propagation direction of resonant standing waves in the samples. Finally, the position of P3 nearly coincides with the temperature at which resonance peaks (for both sample 1 and sample 2) disappear, a local flip mode might therefore be implicated in this loss mechanism as well.

In principle, the RUS data can also be used to determine if elastic waves are coupled to the flip mode. If this is the case, the microstructures would be dynamic in the MHz frequency regime and the effects will be seen in Cole–Cole plots. A Cole–Cole plot is a plot of the real component versus imaginary component of the amplitude of a sample resonance peak. These components correspond to the in-phase and out-of-phase signals from the receiver transducer. If the Kramers–Kronig relationship is fulfilled, a Cole–Cole plot forms a circle [26–28]. Changes in the temperature, pressure, or other experimental variables may rotate the circle as a result of an interaction with an adjacent resonance peak, which could be associated with the alumina rods or the sample. Another source of the phase shift is dynamical microstructures in the sample, as shown in the cubic phase of BaTiO3 with RUS measurements [28]. However, the phase angles for mechanical resonances determined using the spectra presented in figure 1 show no significant variation that could be related to dynamic microstructures.

Finally, the possibility of polar nanostructures in the paraelastic and ferroelastic phases was investigated using RPS on Pb3(PO4)2. Measurements performed at temperatures between 400 and 550 K show no mechanical resonance peaks that could be associated with the sample or alumina rods. Thus, RPS measurements find no evidence of piezoelectric behavior in Pb3(PO4)2.

4. Discussion and conclusions

RUS measurements on Pb3(PO4)2 show significant softening of the effective elastic constants at Ttrans. The smooth softening is similar to that observed in pseudoproper ferroelastic materials, which stems from bilinear coupling between the order parameter Q and spontaneous strains [29]. However, the $R^3m \rightarrow C2/c$ transition in Pb3(PO4)2 is improper ferroelastic. In this case, the active representation of the order parameter of the transition is associated with the L points on the Brillouin zone boundary and does not possess the same symmetry properties as the symmetry breaking spontaneous strains [29]. Bilinear coupling between the order parameter and spontaneous strains is not allowed by symmetry. Instead the coupling is linear in strain and quadratic in order parameter, in which case the associated elastic constant is expected to remain constant above the transition temperature [9, 29]. One possible mechanism for the observed softening is coupling of acoustic phonons with fluctuations related to the soft optic mode and this is characteristically described in terms of a power law

$$\Delta C = A(T - T_c)\kappa$$  \hspace{1cm} (1)

where $\Delta C$ is the amount of softening, $A$ is a constant, and $T_c$ is the critical temperature (below $T_{\text{trans}}$). The exponent $\kappa$ is expected to have values between $-0.5$ and $-1.5$, depending on the dimensionality of the soft mode [29–31]. For a one-dimensional acoustic mode $\kappa$ is $-0.5$ whereas for two- and three-dimensional soft modes it is $-1.0$ and $-1.5$. Since the squared frequency of a mechanical resonance is proportional to the elastic modulus, we fitted equation (1) to the data for elastic softening $\Delta C \sim \Delta \omega_1^2 = \omega_1^2(T) - \omega_1^2(T = 700 \text{ K})$, with $\omega_1^2(T = 700 \text{ K}) = 45200 \text{ kHz}^2$, where $\omega_1$ is a mechanical resonance of sample 1. In the fitting procedure using equation (1), physically plausible fit parameters were obtained only for values of $\kappa \sim -0.5$. In addition, the critical temperature is found to be $T_c = 453.7 \text{ K}$, within $\sim 0.1 \text{ K}$ of $T_{\text{trans}}$ according to specific heat measurements [6]. Therefore, imposing $\kappa = -0.5$ and $T_c = 453.7 \text{ K}$, we obtain a fit of equation (1) for $\Delta C$ shown in figure 5(a), with $A = 37646 \text{ kHz}^2$. The effect of thermal expansion is also taken into account during the fitting, as explained in the caption of figure 5. As seen in figure 5(a), the power law sufficiently describes the softening of the effective modulus down to $T_{\text{trans}}$.

As discussed in the introduction, the phase transition in Pb3(PO4)2, in addition to a displacive component from the L point soft optic mode, involves order–disorder movements of Pb ions around the threefold axis in the paraelastic phase to break the threefold symmetry and yield microstructures containing locally monoclinic domains in the rhombohedral matrix between $T_{\text{trans}}$ and $\sim 563 \text{ K}$ or locally reoriented monoclinic regions within macroscopic monoclinic twin domains between $T_{\text{trans}}$ and $\sim 430 \text{ K}$. As with polar nanoregions in the relaxor phase Pb(Mg1/3Nb2/3)O3 [32], the precursor behavior for the phase transition itself may then actually relate to these dynamic domain structures and their tendency to freeze below some temperature, giving a pattern of elastic softening which might be more accurately represented by the Vogel–Fulcher relationship

$$\Delta C = A \exp \frac{U}{k_B(T - T_{\text{VF}})}$$  \hspace{1cm} (2)

where $A$ is a constant, $E_0$ is an activation energy, $T_{\text{VF}}$ is the freezing temperature and $k_B$ is Boltzmann’s constant. The fit of this expression to the data for $\Delta C \sim \Delta \omega_1^2$, as described for the fit using the power law in equation (1), is shown in figure 5(b). The values for the fit parameters are given in the caption of figure 5. Similarly to the power law, a Vogel–Fulcher relationship is also compatible with the precursor softening. Thus a classic displacive one-dimensional soft mode (figure 5(a)) is possible, but strong short range ordering with domains of off-centered Pb ions leading to glass-like states cannot be excluded (figure 5(b)). Compatibility of both expressions is consistent with the transition mechanism described in [9], where a displacive soft mode is found to couple with the flip mode. There is no evidence in the precursor regime for acoustic loss, however, which is most likely due to the very high frequency of the flip mode, $\sim 10^{10} \text{ Hz}$, compared to the kHz–MHz frequency range of the RUS measurements.
While the overall softening observed by RUS, Brillouin scattering, and DMA are similar above \( T_{\text{trans}} \), the elastic behavior obtained using three techniques shows significant differences in the stability field of the monoclinic phase (figure 3). The gross differences are understandable in terms of the specific properties of the ferroelastic twin walls, whose mobility gives rise to strong (superelastic) softening and strong attenuation. These specific properties have a relatively slow characteristic relaxation time (motion usually on a frequency scale of Hz not MHz) and the requirement for a relatively large stress to unpin the needle tips from pinning points. The stress conditions in an RUS experiment are not known, but Walsh et al. [33] and Carpenter et al. [34] have estimated that the induced strains would be on the order of \( 10^{-7} \), in comparison with \( 10^{-4} - 10^{-6} \) in DMA. Thus, in the light of the small peak in \( Q^{-1} \) at \( T_{\text{trans}} \), interfaces between rhombohedral and monoclinic phases in a small temperature interval of coexisting phases at the (first order) phase transition appear to be sufficiently mobile to give rise to measurable anelastic losses under the same conditions. While for the resonances of sample 2 the return of \( Q^{-1} \) to low values immediately below \( T_{\text{trans}} \) implies immobile twin walls, the high losses experienced by the resonances of sample 1 below \( T_{\text{trans}} \) (figure 1) indicate that twin walls between monoclinic domains are mobile even at RUS frequencies and low levels of stress. The different behavior for sample 1 and 2 shows that the mobility of twin walls depends on, apart from the frequency, their orientation with respect to the direction of propagation of elastic resonant waves.

Explaining why the RUS peaks fade into the background below about 430 K (for both sample 1 and sample 2) is a bit more problematical. Although it was not commented on in the original paper of Torres et al. [14], there is perhaps a small step in the Brillouin scattering data for \( C_{66} \) at about the same temperature (figure 3) and this temperature is known to be significant from other measurements [4, 7, 10, 11, 13, 35]. In particular, there is a change in the evolution of the volume strain [4, 13]. Salje et al. [4] have proposed that the dynamical reorientation of microdomains of the locally monoclinic structure within the rhombohedral phase between \(~530\) and \(453\) K, continues between \(453\) and \(~430\) K, but as dynamical reorientation of local domains within the monoclinic structure. These clearly do not couple with acoustic modes under RUS conditions either above or immediately below \( T_{\text{trans}} \), but their disappearance below \(~430\) K coincides with the increase in acoustic dissipation. The simplest explanation is then that they effectively freeze out with relaxation times which fall into the kHz–MHz range below this temperature.

Finally, RPS measurements at temperatures between 400 and 550 K show no evidence of macroscopic or microscopic polarization in \( Pb_3(PO_4)_2 \). The absence of polarity in the paraelastic phase confirms that the low-temperature space group is \( C2/c \) rather than noncentrosymmetric \( C2 \) as reported by Kiat et al. [15]. In addition, the results are consistent with Bleser et al. [16], who have determined that the SHG signals detected in paraelastic and ferroelastic phases are due to oxygen defects, which break local inversion symmetry and create polar nanostructures. Since these polar nanostructures are randomly located throughout the sample, they are not correlated, which explains why no RPS signal is observed in \( Pb_3(PO_4)_2 \).

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Figure 5. Fits to the data for elastic softening about \( T_{\text{trans}} \) using (a) equation (1) for power law dependency, and (b) equation (2) for the Vogel–Fulcher relationship. For the power law, \( \Delta C \sim \Delta \omega_0^2 = A(T - T_e)^\gamma + a + bT \), the fit parameters are \( A = 37,646\) kHz\(^2\), \( T_e = 453.7\) K, \( \kappa = -0.5\), \( a = 4,206\) kHz\(^2\), and \( b = -10.12\), where \( a + bT \) is used to account for thermal expansion. For the Vogel–Fulcher relationship, \( \Delta C \sim \Delta \omega_0^2 = A \exp(U/\{T - T_{\text{VF}}\}) + a + bT \), where the constant \( \kappa \) is suppressed, the fit parameters are \( A = 1838\) kHz\(^2\), \( T_{\text{VF}} = 411\) K, \( E_s = 97.3\) K. For consistency, the same values for \( a \) and \( b \) were used as those used in the fit for the power law.
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