Low energy excitations in crystalline perovskite oxides: Evidence from noise experiments

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Abstract

In this paper we report measurements of 1/f noise in a crystalline metallic oxide with perovskite structure down to 4.2K. The results show existence of localized excitations with average activation energy ≈ 70-80 meV which produce peak in the noise at T ≈ 35-40K. In addition, it shows clear evidence of tunnelling type two-level-systems (as in glasses) which show up in noise measurements below 30K.

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A number of solids exhibit excitations which are of much lower energy than the characteristic energy scale of typical lattice excitations. Most of the time the low energy excitation arises from defect motions where atoms or group of atoms have more than one equilibrium configurations of almost equivalent energy separated by shallow barriers which are accessible by tunneling or thermal activation. A particular type of such defect motions are atomic or molecular tunneling of defects seen in a number of doped crystalline systems[1,2]. In case of glasses and other amorphous solids the tunneling centers are of a special kind(popularly called Two Level Systems) which give rise to the Universal low temperature properties of glasses[3]. This particular field has been well studied by a number of techniques. Recently, very sensitive torsional oscillator experiments have been used to study the evolution of low energy excitations in amorphous silicon[4]. It has also been known for some time that certain crystalline solids including metals and metallic alloys show glass-like low energy excitations[5]. In this communication we report existence of low energy excitations in three dimensional cubic perovskite oxides which were observed through sensitive noise experiments.

It has been known since a decade that the cuprate superconductors (belonging to perovskite class) and perovskites with ABO_3 structure can posses "glass-like" low energy excitation originating from oxygen defects[6]. In recent years, as the quality of the high T_c crystals and films improved, the observed magnitude of these excitations have become less, often falling far short of the detectability of the techniques used, like specific heat.

We have undertaken this experiment to investigate the following issues: (i) to establish that existence of low energy excitations may be generic in ABO_3 type perovskite oxides and (ii) to establish that noise experiments can detect such excitations which cannot be detected by other techniques. In particular, the existence of low energy excitations in epitaxial films of perovskite oxide will have implications on the transport properties and is a new addition to our knowledge of oxygen dynamics of these materials. To our knowledge this is the first experimental determination of noise in normal conducting perovskite oxides down to low enough temperature so that the low energy excitations can be detected.

The choice of the material for our study is $LaNiO_{3-\delta}$. This is a perovskite oxide with

almost cubic structure[7]. It is electrically conducting in stoichiometric form ($\delta \approx 0$). A number of experiments (including noise experiments) show that the oxygen is highly mobile in this oxides when $\delta \approx 0$. Under normal pressure the oxygen diffuses out of the system even at room temperature and δ increases as observed recently through sensitive noise experiments[8].

Electronic transport in this system is strongly linked to oxygen stoichiometry(δ) and resistivity(ρ) increases sharply as δ increases[9]. This makes electronic conduction noise a very sensitive probe of oxygen dynamics in this solid. In a previous study[8] we have shown that noise experiments can detect long range oxygen diffusion for T¿150K. In this paper we show that there exists clear evidence of low energy excitations in these solids which most likely arises from localized dynamics of "frozen defects" of the oxygen lattice at lower temperatures (T¡100K). It is not necessary however, that these excitations can be called "glass like".

Epitaxial films of $LaNiO_{3-\delta}$ with nominal thickness $\approx$ 150 nm were deposited on $LaAlO_3$ substrates by pulsed laser deposition (PLD) using excimer laser. The details of film preparation is given elsewhere[16]. The epitaxy of the films are tested by X-ray diffraction. The resistivity of the film was measured by a four probe technique over the temperature range 4.2K¡T¡380K. The film used by us had $\rho_{RT} \approx 0.6$ mΩ-cm and $\rho_{4.2K} \approx 0.25$ mΩ-cm and an estimated $\delta \approx 0.05$. This is close to but somewhat larger than the resistivity obtained in best bulk samples prepared by high pressure oxygen treatment[17].

The noise was measured by a five probe ac technique (carrier frequency 377 Hz) using samples of bridge type configuration with active volume for noise detection (Ω) $\approx 5\times 10^{-8}$ cm^3 with peak current density $\sim 10^4$ A/cm^2. The noise determination used digital signal processing techniques described elsewhere[10]. The temperature control during noise determination was better than 10mK. The background noise primarily consisted of Johnson noise $4k_BTR$ from the sample. Quadratic dependence of the spectral power density $S_v(f)$ on V_{bias} ensured ohmic character of the noise.

To normalize our data taken at different frequencies we use a quantity(γ/n) defined as[12]:

$$\gamma/\mathrm{n} = \mathrm{f}\Omega \mathrm{S}_v(\mathrm{f})/\mathrm{V}_{bias}^2 \quad (1)$$

where n is the carrier density, $S_v(f)$ is the spectral power density at frequency f measured with bias V_{bias}. This is justifiable given the fact that $S_v(f) \propto V_{bias}^2$ and it has nearly 1/f dependence. [In general $S_v(f)$ has $1/f^{\alpha}$ dependence with the exponent close to 1] We express our results as γ/n because there are uncertainties in exact value of the carrier concentration n.Such uncertainties however do not affect the main conclusions of this work. The quantities on the right hand side are all experimentally measurable. In fig.1 we show the normalized power (γ/n) as a function of temperature at three frequencies. A few plots of typical noise spectra are shown in fig.2a. The spectra are shown as $S_v(f)$ vs. f to accentuate the deviation of α from 1. Beyond 60K noise increases monotonically with T. The rapid increase of γ/n above 150K is associated with long range oxygen diffusion. This particular issue has been discussed previously[8]. In this brief report we focus the region T¡60K where the long range diffusion has ceased.

Below 60K there are distinct peaks in noise power as a function of T. The peak positions as well as the peak heights of both the peaks depend on the measuring frequencies. The peak positions shift to higher temperatures with increasing frequency which we interpret as a signature of thermally activated process. From fig.2 we can also see that there is a perceptible change in α as we cross the peak region.

If a thermally activated process with a characteristic time scale τ governs the underlying dynamics associated with the distribution of the electron scattering centers, it can give rise to excess noise in the frequency scale $\sim 1/\tau$. Dutta-Horn model envisages such thermally activated centers as the origin of $1/f^{\alpha}$ noise provided the activation energy has a broad distribution with respect to $k_B T$[13]. As we see from fig.1 for T¡35K the noise magnitude decreases rather slowly with decreasing temperature which requires a broad ($\gg$kT) distribution of activation energies at these temperatures. It is this observation that has prompted us to use the Dutta-Horn theory to extract the density of states(DOS) D(E) in the dynamics of the scatterers from the observed temperature variation of γ/n. In the framework of the Dutta-

Horn model, the energy E is related to τ through the relation $\tau = \tau_0$ exp[E/k_BT], τ_0^{-1} being the attempt frequency. The value of τ_0 ($\approx 3\times10^{-11}$ sec) was obtained from the shift in peak temperatures for different observation frequencies. We show in fig.3 the result of calculation of D(E) based on this model. In this model E $\approx$ -k_BTln($\omega\tau_0$) where $\omega = 2\pi$f is the measuring frequency. We find that the measurements of γ/n for all the three frequencies give D(E) that peak around 70$\pm$4 meV and 84$\pm$10 meV. To check the self-consistency of the analysis we calculated the exponent (α) at 5Hz from the observed spectra at different temperatures and compared the values with that predicted by the Dutta-Horn model (fig.2b). We used the relation α = 1 - (∂lnS/∂lnT - 1)/ln($\omega\tau_0$). ∂lnS/∂lnT was calculated from a smooth curve fit to the experimental data. It is cear from the figure that observed α agrees well with the prediction. Thus the analysis of the spectra in the framework of the Dutta-Horn model points to the existence of a broad flat spectrum of low energy relaxing states accompanied by two distinct peaks.

$LaNiO_3$ belongs to ABO_3 class of perovskite oxides in which the oxygen is the mobile species and defect chemistry plays an important role[14]. The oxygen diffusion in this material is mediated by defects like oxygen vacancy and has an activation energy $\sim$ 1eV[8]. In the temperature range of our interest the long range diffusion is frozen. Only kinetics that seems to be allowed is local relaxation involving oxygen and oxygen-vacancy combination. The important question however is that the observed average activation energy $\langle$E$\rangle$ for this process is $\approx$ 70 meV which is more than an order of magnitude less than that seen for long range diffusion. Typical Θ_D of this oxide found from specific heat as well as Bloch-Gruneissen theory is $\approx$ 350K - 400K which shows the scale of typical lattice vibration to be smaller than the activation energy associated with the peaks. Thus the activation energy seen by us has an energy scale in between the lattice vibration scale and the activation energy associated with long range diffusion. Also there seems to be a split peak in D(E) with activation energy differing by approximately 10 meV implying that there are two classes of oxygen defect sites with slightly differing activation energy. Two such different sites can arise if the structure is

slightly distorted from the cubic structure.These small distortions from cubic structure do exist in these oxides[7]. Our noise experiments thus clearly show the existence of low energy localized excitation in this solid. In the following we will investigate the region with E $\leq$ 60 meV.

We find from the D(E) vs. E curve that while D(E) $\rightarrow$ 0 for E $\geq$ 100 meV, there are substantial number of states left with much lower energy and D(E) $\rightarrow$ Constant for E $\leq$ 60 meV. It raises the probability of existence of a glass-like excitations in these crystalline solids with nearly constant density of states. To investigate this point further we continued the measurement down to T $\approx$ 4.2K. We find that below 30K the magnitude of the noise is $\propto$ T as seen in the inset of fig.1. At T ¡ 30K, defect relaxation by thermally activated processes freeze out because the relaxation time τ becomes very large. A likely mechanism that can give rise to such low energy processes at low temperature is tunnelling of atomic or molecular species as were found in certain doped alkali halide systems[1]. It has been shown before that in presence of random strain fields such two level tunnelling defects can broaden out to give tunnelling states with a broad energy spectrum[2,11]. It has been shown theoretically that the temperature dependent relaxation rates of the tunneling states (arising from interactions with both electrons and phonons) lead to fluctuations in the number density of these states[15].

It is known that the tunneling systems in glasses can interact with the electrons and thus provide an extra scattering mechanism. The fluctuation in the equillibrium number density of the tunneling states thus gives rise to a fluctuation in the electron scattering rate leading to noise in the electrical resistivity. The noise power spectrum of this process measured over a volume Ω is given as[15],

$$\frac{S_v(f)}{V^2} = \frac{\langle C^2 \rangle}{n_{imp}^2} \frac{\pi D_{TLS}}{\Omega} \frac{k_B T}{\omega} \tag{2}$$

where D_{TLS} is the constant density of states of the TLS, $\omega = 2\pi$f, C is a dimesionless coupling constant $\sim 10^{-2}$ and n_{imp} is the concentration of impurities which scatter electrons. This will give rise to a normalized spectral power

$$\frac{\gamma}{n} = \frac{1}{2} \langle C^2 \rangle k_B T \frac{D_{TLS}}{n_{imp}^2} \tag{3}$$

Our experimental observation for T ¡ 30K (inset of fig 3) show a clear linear dependence on T as mentioned before and the power spectra are also 1/f type. This we consider as an evidence for existence of glass-like low energy excitations in these oxides. Taking n_{imp} as the number density of oxygen vaccancies (our sample has $\delta \approx 0.05$) we obtain $D_{TLS} \sim 10^{35}$ erg^{-1}cm^{-3}. This assumes every impurity atom is associated with a TLS. However, in glasses and low doped alkali halides it is known that the TLS arises from a group of impurity atoms and $n_{imp} \ll$ oxygen defect density. In that case $D_{TLS} \ll 10^{35}$ erg^{-1}cm^{-3}. A $D_{TLS} \approx 10^{31}$-10^{33} erg^{-1}cm^{-3} is found in oxide glasses[3].

In order to cross-check whether the flatness of the DOS at low energies is a necessary condition to explain the observed temperature dependence of noise, we carried out calculations of the noise magnitude as a function of temperature with several trial DOS. Assuming an activated scattering mechanism we can write[13],

$$S(f,T) = \int_0^\infty D(E) \frac{2\tau_0 e^{E/kT}}{1 + (2\pi f \tau_0)^2 e^{2E/kT}}\, dE \tag{4}$$

We find that usual bell shaped DOS with width $\gg$ kT does not produce the observed temperature dependence of noise particularly at lower temperatures. Best fit to the data was obtained with DOS that have a flat distribution D(E) $\approx$ constant for E ¡ 70 meV. In fig.4 we have shown the calculation based on two typical choices of DOS as examples. The dotted line is calculated from a Lorenzian D(E) having width of $\approx$ 15 meV and the solid line is obtained from a Lorenzian with flat and finite low energy tail (inset of fig.4). The need for a flat low energy distribution is clearly visible. Thus our analysis shows that if we satisfy two basic requirements we can reproduce our data. These two requirements are (a) a collection of TLS with a broad distribution and (b) a flat DOS at low energy. Apart from these two general aspects there is nothing unique about the choice of the DOS.

In these perovskite oxides the electronic path is formed by the network of transition metal and oxygen where the transition metal is at the center of the octahedron formed by six oxygen ions. The electrical conduction is strongly modified by any defect in the oxygen lattice. The noise is thus a very sensitive probe of oxygen and oxygen-defect dynamics which

directly couples to the scattering centers which give rise to electrical resistivity and resulting $1/f^{\alpha}$ noise. The low energy defects seen through the noise experiments arise from the oxygen dynamics in the three dimensional transition metal-oxygen-transition metal network. All ABO_3 oxides in particular has such networks. It may thus happen that the low energy excitations seen in $LaNiO_3$ is generic to all such ABO_3 oxides. In high T_c cuprates, however, there are different types of chain and plain oxygens. It will not therefore be proper to comment on existence of low energy excitations in cuprates based on measurements on $LaNiO_3$.

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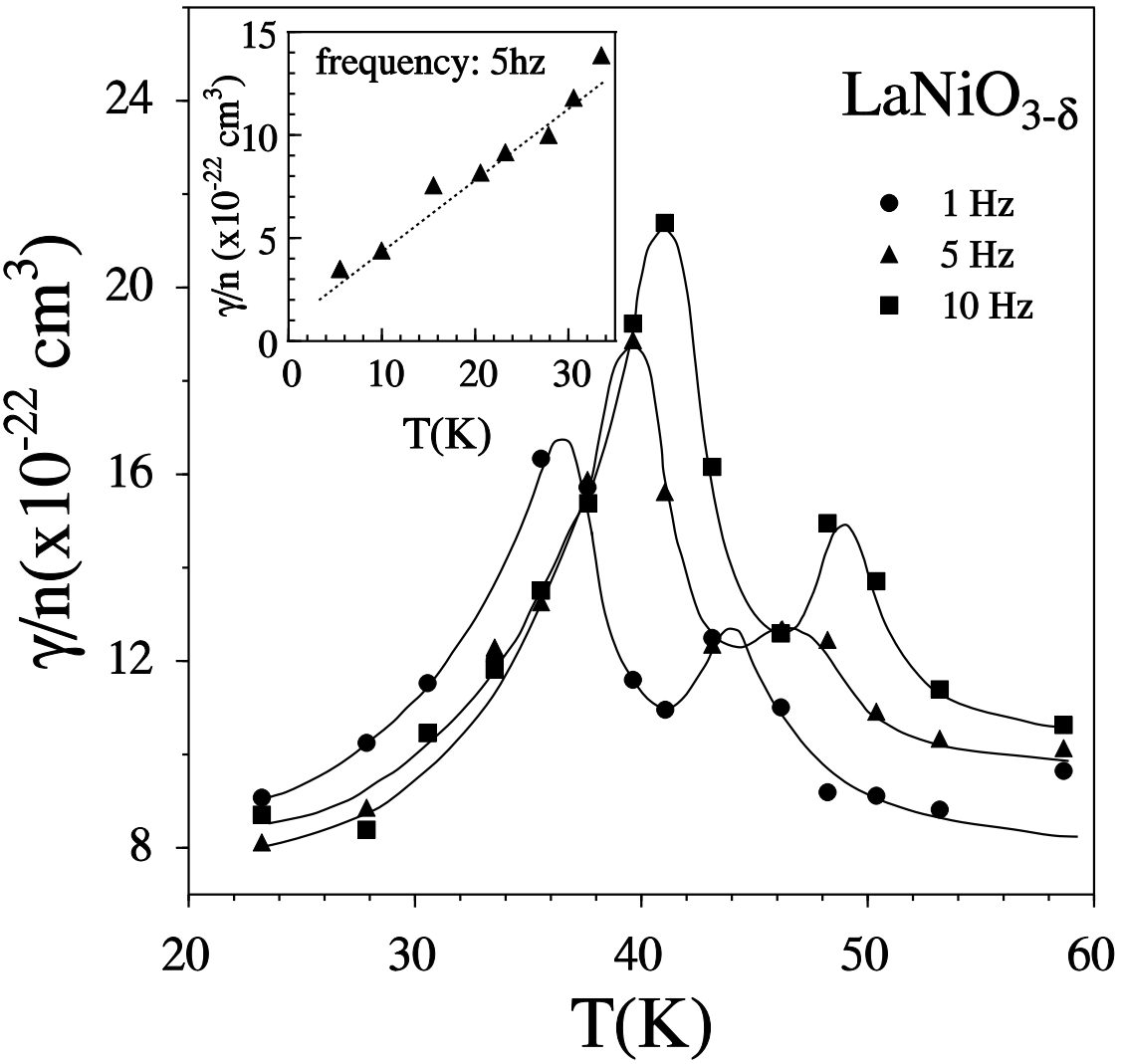
Figure Caption

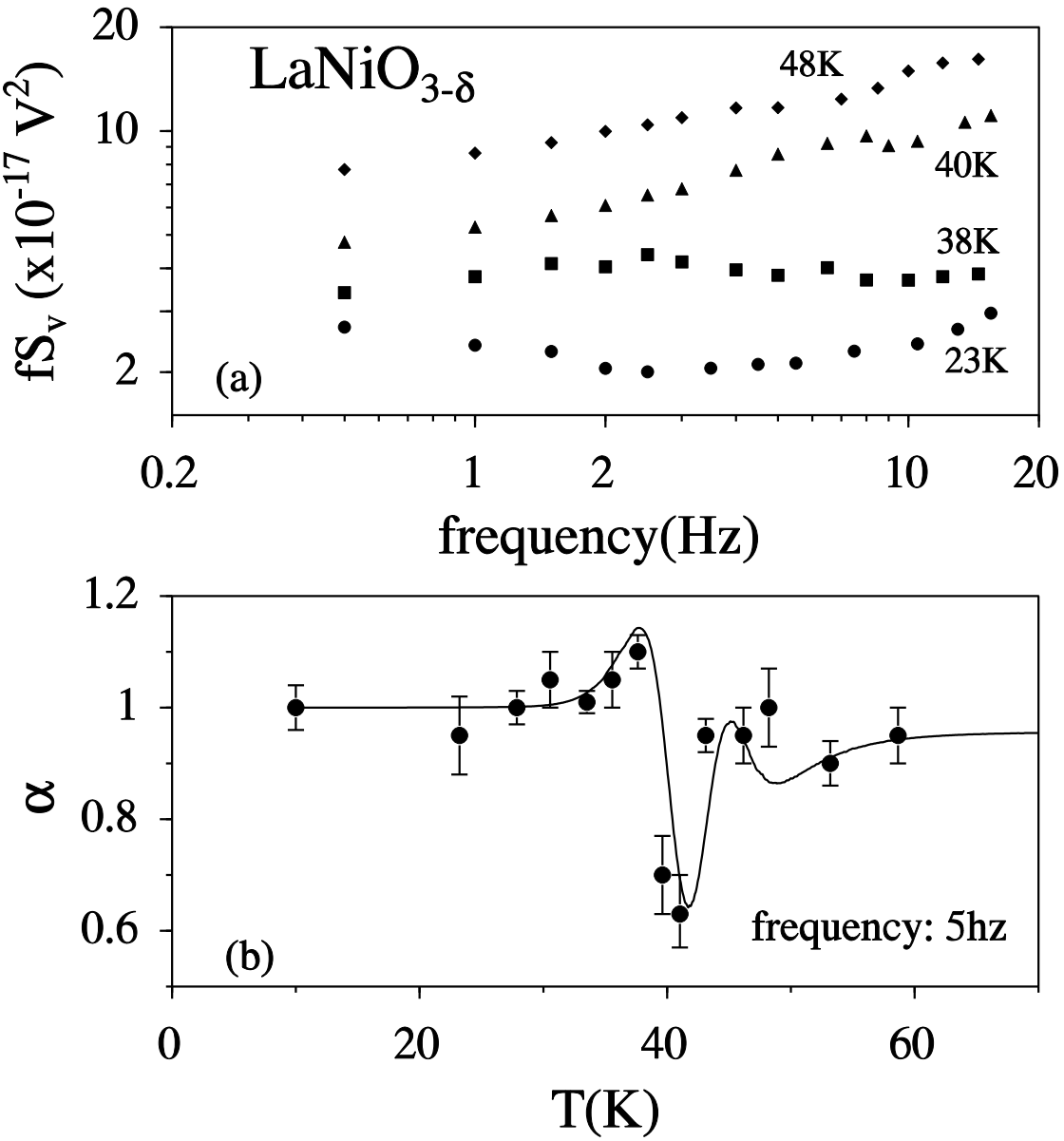
Fig.1. Temperature dependence of the normalized noise power (γ/n) at low temperature at three measuring frequencies. The solid lines are guide to the eye. The inset magnifies the low temperature (T ¡ 35K) tail of the noise magnitude.

Fig.2. (a) Plots of the noise power at four different temperatures. Spectra at different temperatures are shifted for clarity. (b) Temperature variation of the spectral slope at 5Hz. The solid line is the prediction of the Dutta-Horn model obtained from the smooth curve fit to the noise magnitude (see fig.4).

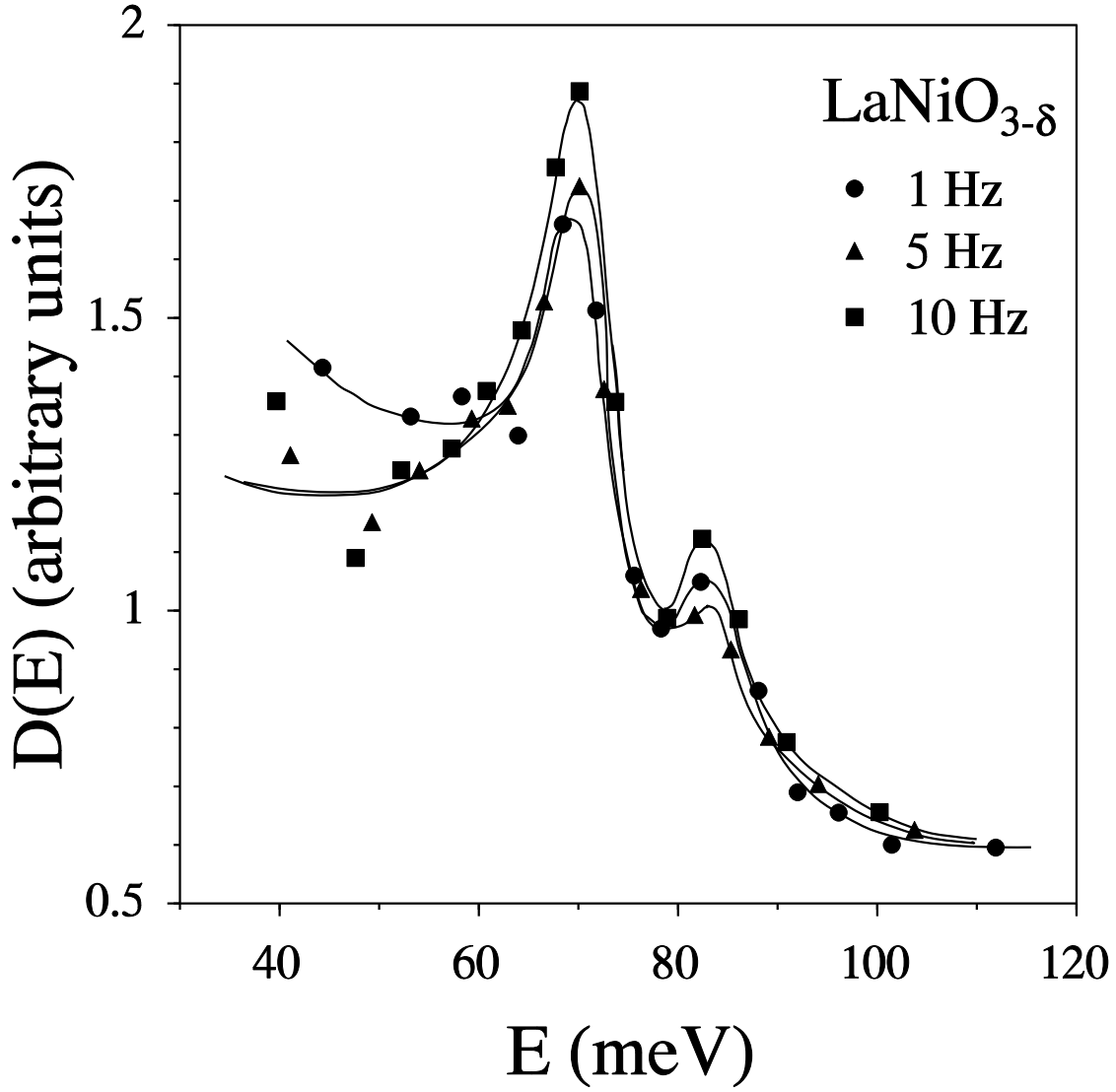
Fig.3. Distribution of activation energy E obtained from the data using Dutta-Horn model. Value of $\langle\tau_0\rangle$ (=3×10^{11} sec) is obtained from the shifting of the noise peak for different observation frequency. The solid lines are guide to the eye.

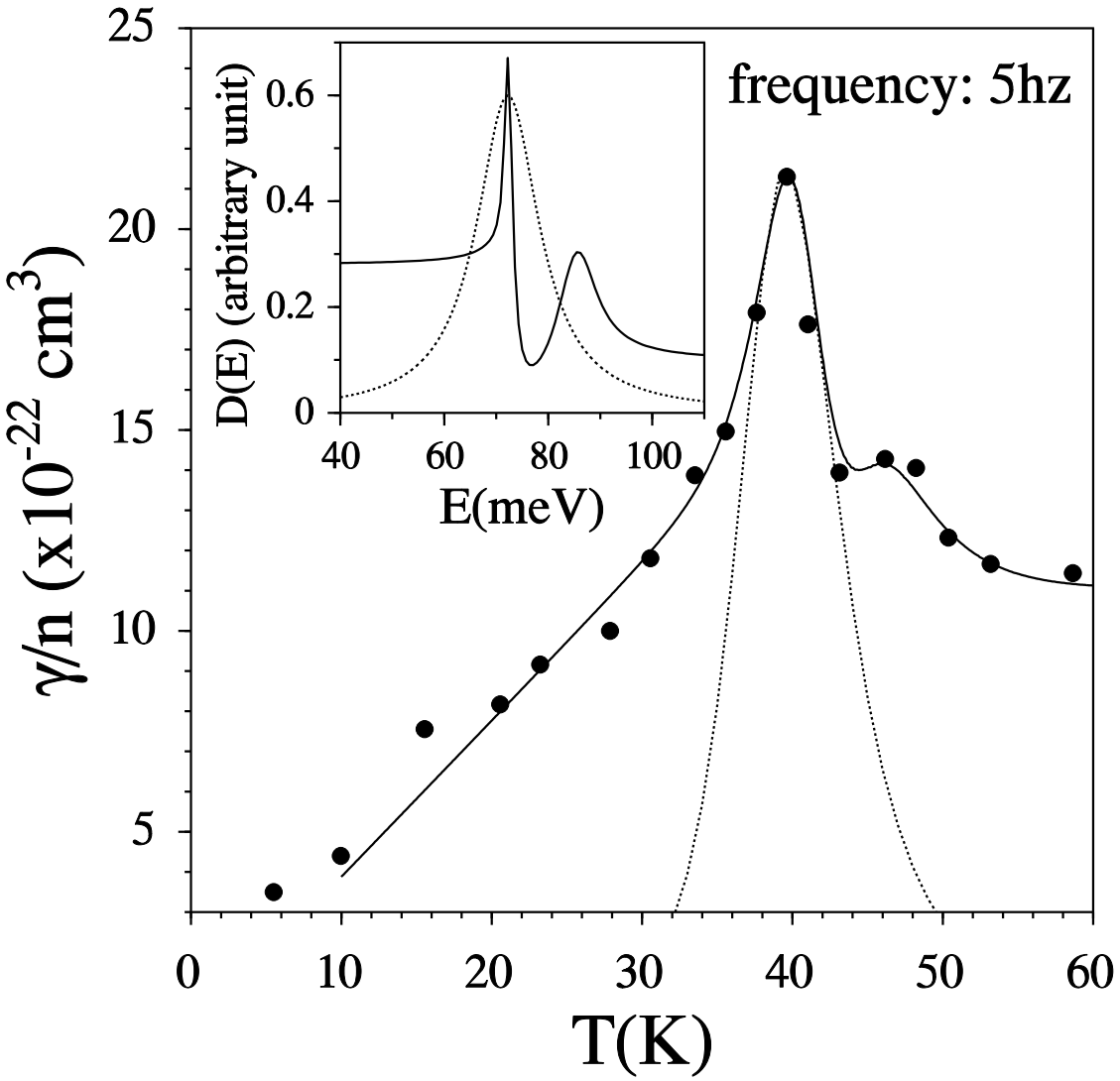
Fig.4. Calculated noise at 5Hz from trial DOS. The solid line fit to the data corresponds to the DOS shown in the inset (solid line). The dotted line is evaluated from a Lorenzian DOS (for details see text).


LaNiO3-δ
1 Hz
5 Hz
10 Hz
γ/n(x10-22 cm3)
T(K)
frequency: 5hz
γ/n (x10-22 cm3)
T(K)


LaNiO3-δ
48K
40K
38K
23K
(a)
fSv (x10-17 V2)
20
10
2
0.2
1
2
10
20
frequency(Hz)

(b)
frequency: 5hz
α
1.2
1
0.8
0.6
0
20
40
60
T(K)


LaNiO3-δ
1 Hz
5 Hz
10 Hz
D(E) (arbitrary units)
E (meV)
2
1.5
1
0.5
40
60
80
100
120


frequency: 5hz
γ/n (x10^-22 cm^3)
T(K)
D(E) (arbitrary unit)
E(meV)
0
5
10
15
20
25
0
10
20
30
40
50
60
0
0.2
0.4
0.6
40
60
80
100