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Using the dielectric constant and conductivity at microwave frequency, we study the differences between highly conducting polyacetylenes and standard metals. We report that the microwave dielectric constant at room temperature for heavily-iodine-doped Tsukamoto polyacetylene films is negative and very large. This demonstrates that the highly conducting state is metallic despite the decrease in conductivty with decreasing temperature. The anomalously long transport time is attributed to suppression of both phonon and impurity backward scattering in a structure with an open Fermi surface. We analyze the temperature-dependent data using a model of three-dimensional metallic fiber segments coupled by weak links within which one-dimensional localization effects occur.

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Metallic Microwave Dielectric Response of Polyacetylene

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Abstract

Using dielectric constant and conductivity at microwave frequency, we study the differences between highly conducting polyacetylenes and standard metals. We report that the microwave dielectric constant at room temperature for heavily-iodine doped Tsukamoto polyacetylene films is negative and of record size. This demonstrates that the highly conducting state is metallic despite the decrease in conductivity with decreasing temperature. The anomalously long transport time is attributed to suppression of both phonon and impurity backward scattering in a structure with an open Fermi surface. We analyze the temperature dependent data using a model of three-dimensional metallic fiber segments coupled by weak links within which one-dimensional localization effects occur.

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Though traditional metals (conductivities of 10^4 to 6×10^5 S/cm) have been studied for more than a century, conducting polymers have been investigated for only the past one and a half decades. Doped polyacetylene [$(\mathrm{CH})_x$] has been the prototype system since the initial report of the achievement of a conductivity of $\sigma \sim 100$ S/cm upon doping with iodine and other donors and acceptors [1]. In addition to their modest conductivities conducting polymers differed from usual metals in that their conductivities decreased with decreasing temperature (T), becoming insulators at low temperatures. Despite the nonmetallic $\sigma(T)$, their T-independent Pauli susceptibility [2] and a linear dependence of thermoelectric power on T [3] are metal-like.

There is renewed interest in the highly conducting state of conducting polymers with the advent of improved chemical processing resulting in doped polymers of conductivities of $\sim10^4$ S/cm and even higher values [4–9]. Yet the conductivities of even these new conducting polymers decrease as the temperature is lowered [4,6,7,9] (for a few samples the conductivities are reported to become constant for $T <\sim 10K$ [6]). This unusual behavior has attracted attention. One explanation of the unusual $\sigma_{dc}(T)$ could be the Anderson disorder driven metal-insulator transition [7,9–11]. However, the Ioffe-Regel criterion [12] requires a degree of disorder such that the mean free path is comparable with the Fermi wavelength: small τ_{tr}, where τ_{tr} is the total transport time. For standard metals, this criterion corresponds to very strong disorder and hence very low σ_{dc}. This mechanism is unlikely for the chain structured and substantially crystalline conducting doped $(\mathrm{CH})_x$.

In contrast to the substantial disorder required for localization in three-dimensional (3d) systems, Mott and Davis pointed out that in a one-dimensional (1d) conductor the localization of carriers arises even for weak disorder because of the strong quantum interference caused by impurity scattering [13]. With decreasing temperature the 1d localization effects become pronounced; the interplay between the impurity and the phonon scattering leads to the observed T-dependence of conductivity. Within this model the charge delocalization of the entire system at $T = 0$ is determined by interfibril coupling and intrafibril disorder [8]. This model is in agreement with the observed weak T-dependence of σ_{dc} of doped $(\mathrm{CH})_x$ [6].

However, there has been a lack of convincing evidence of the intrinsic metallic behavior of charge carriers even at room temperature (RT), as well as estimates for the transport-time (τ_{tr}) and whether they are long enough to provide high σ_{dc} and at the same time appreciable localization effects.

It is clear that additional probes are necessary to elucidate the appropriate description of the highly conducting state of these polymers. Measurement of the dielectric constant (ϵ_{mw}) at microwave frequencies ($10^9 - 10^{10}$ Hz) provides a direct probe of the ability of an electronic system to follow a time varying applied field. For electrons localized to a length L_{loc}, ϵ is positive and proportional to L_{loc}^2. In marked contrast, for metals ϵ is negative and very large (typically $|\epsilon| \geq 10^5$) for frequencies much below a plasma frequency, ω_p, with $\omega_p = 4\pi ne^2/m^*\epsilon_b \sim$ several eV for most usual metals [14]. Here n is the delocalized conduction electron concentration, e is the electron charge, m^* is the effective mass, and ϵ_b the background dielectric constant. From the Drude model [15], at low frequencies ($\omega \ll \omega_p$), the ratio of $|\epsilon/\sigma| \simeq \tau_{tr}/4\pi$ provides a direct measure of the relaxation time at the microwave frequency.

In this Letter we report the results of a simultaneous study of the microwave frequency (6.5×10^9 Hz) transport and dielectric properties of very highly conducting iodine doped $(CH)_x$ compared to those of a standard metal (Nb) to address the mechanism of the metallic conductivity of doped polyacetylene. A huge negative microwave dielectric constant ($\epsilon_{mw} \sim -1.7 \times 10^6$) is determined for heavily iodine doped six-fold stretched Tsukamoto $(CH)_x$ [T-($(CH)I_{3y})_x$] with a smaller value ($\sim -3.9 \times 10^5$) determined for unstretched material. These values are similar to that reported here for ϵ_{mw} of Nb ($\sim -4.0 \times 10^6$) and by Ordal *et. al.* for other standard metals [14]. However, while for standard metals ϵ_{mw} becomes increasingly negative and microwave conductivity (σ_{mw}) increasingly positive with decreasing temperature, for T-$[(CH)I_{3y}]_x$ $|\epsilon_{mw}|$ and σ_{mw} decrease with decreasing temperature. A Drude analysis of ϵ_{mw} and σ_{mw} yields a small plasma frequency $\omega_p \sim 200$ cm^{-1} (in agreement with optical data) and a transport time τ_{tr} of $\sim 3.3 \times 10^{-11}$ sec, long compared to that of standard metals (e.g., $\tau_{tr} \sim 5 \times 10^{-12}$ sec for Nb films). We analyze the T-$[(CH)I_{3y}]_x$

data within a model of metallic polymer fiber segments (composed of many parallel chains) with long relaxation times coupled by weak links within which 1d localization effects occur. We address the change of dielectric properties of doped T-$(CH)_x$ with aging.

A detailed description of the chemical processing of T-$(CH)_x$ has been reported previously [4]. The microwave cavity perturbation (MCP) technique [16] was used for the measurement of $\epsilon_{mw}(T)$ and $\sigma_{mw}(T)$. The MCP method is excellent for air sensitive materials because of the absence of electrical and mechanical contacts, and because the sample holder can be easily moved into a glove box preventing the exposure of the sample to air. The thickness of Nb film sputtered onto glass was less than the skin depth at the measurement frequency.

Figures 1 and 2 show the microwave dielectric constant and conductivity, respectively, as a function of temperature for center portions of heavily-iodine doped six-fold stretched and also unstretched T-$(CH)_x$ samples. The insets are the results for Nb film. The ϵ_{mw}(RT) and σ_{mw}(RT) of the stretched samples are -1.7×10^6 and 4700 S/cm, respectively, while the values for the unstretched samples are $\epsilon_{mw} \sim -3.9 \times 10^5$ with $\sigma_{mw} \sim 1000$ S/cm. These values compare well to $\epsilon_{mw} \sim -4 \times 10^6$ and $\sigma_{mw} \sim 5.8 \times 10^4$ S/cm for Nb at RT. The data were reproducible using different samples. The huge negative value of ϵ_{mw} unambiguously allows us to consider heavily-doped T-$(CH)_x$ as a true metal at least at high temperatures and to apply the Drude model. At low frequency ($\omega\tau_{tr} \ll 1$ where ω is the frequency and τ_{tr} is the transport time), $\epsilon \simeq -\omega_p^2\tau_{tr}^2$ and $\sigma \simeq (\omega_p^2/4\pi)\tau_{tr}$ [15]. The ω_p's of stretched and unstretched doped T-$(CH)_x$ are ~0.025 eV ($\simeq$ 200 cm^{-1}) and ~0.012 eV ($\simeq$ 100 cm^{-1}), respectively, at RT. These relatively small plasma frequencies suggest that only the most delocalized electrons of the conduction band, which represent only a small fraction of all electrons, participate in this low frequency microwave response.

The transport time τ_{tr} is estimated to be $\sim3.3\times10^{-11}$ sec for both unstretched and stretched materials as compared with $\sim 5.0 \times 10^{-12}$ sec for Nb. Irrespective of the model used, the ratio $|\epsilon_{mw}(\omega)/4\pi\sigma_{mw}(\omega)| \approx |\frac{d}{d\omega}\ln\sigma(\omega)|_{\omega=0}$ gives the characteristic time scale of relaxation. This value of τ_{tr} is one to two orders of magnitude larger than usual for alkali or transition metals [15] and corresponds to unusually high mobility carriers for a metal. Note that the nearly identical τ_{tr} for both stretched and unstretched samples indicates that the relaxation processes of metallic fibril bundles are not sensitive to stretching.

We suggest that the origin of this anomalously long τ_{tr} lies in the chain and fibrillar structure of $(\mathrm{CH})_x$. Electrons move primarily along the polymer chains which are coupled into fibrils. Their Fermi surface is open as expected for a highly anisotropic material. In this case backward scattering from $\mathbf{k}_F$ to $-\mathbf{k}_F$ is necessary for relaxation of carrier momentum. Disorder and phonons can produce similar scattering. However, these random static scatterers, e.g. dopants, are outside the chains [17,18]. As a result the elastic backward scattering rate (which is given by the $2\mathbf{k}_F$–Fourier component of the random potential) is relatively weak. The inelastic backward scattering is also very weak because of the freezing of the involved high frequency $[\omega(2\mathbf{k}_F)]$ phonons [19]. One expects that the elastic backward scattering dominates the phonon backward scattering in determining the transport time even at RT. This follows from the fact that experimental τ_{tr} remains approximately constant for $T \geq 100K$. Presumably, rare strong defects such as chain interruptions and sp^3 defects determine the total transport time. Degradation of $(\mathrm{CH})_x$ with aging is mainly related to the appearance of such defects.

The decrease of σ_{mw} and ϵ_{mw} with decreasing temperature contrasts with the T-dependencies for Nb. These data indicate that doped $(\mathrm{CH})_x$ is in the weakly localized regime, in apparent contradiction to the huge and negative ϵ_{mw} at RT. Given the long transport time and the polymer crystallinity, the Ioffe-Regel criterion for 3d localization is not met. Hence the localization of doped $(\mathrm{CH})_x$ is likely of 1d origin.

According to Ref. [8] 1d localization persists in fibrillar networks with weak interfibril coupling through individual 1d chains. Similarly 1d localization should arise as charges traverse on uncorrelated chains through the disordered regions seperating crystalline domains. The metallic state at high temperature then results from delocalization via phonons interrupting the quantum interference of the elastic scattering. The initial decrease of ϵ_{mw} and σ_{mw} of highly conducting $(\mathrm{CH})_x$ with decreasing temperature can be explained by phonon-controlled localization effects. Adding the first 1d quantum correction to the Drude term

[11,20],

$$\sigma(\omega) \simeq \frac{\omega_p^2 \tau_{tr}}{4\pi}[1 + i\omega\tau_{tr} - \frac{c_\perp}{\sqrt{-i\omega\tau_{tr} + \tau_{tr}/\tau_{in}(T)}}] . \tag{1}$$

Here τ_{tr} is the scattering time due to static disorder and impurities, and $\tau_{in}(T)$ is the inelastic scattering time which determines the phase-breaking rate. The large phonon forward scattering rate $[1/\tau_{ph}(k \sim 0, T)]$ contributes mainly to $1/\tau_{in}(T)$. The factor $c_\perp$ depends on the interchain coupling inside the fibril and varies from 1 for weak coupling to $1/M$, where M is the number of chains within the fibril for strong coupling [20]. We expect that $c_\perp \ll 1$ in the case of highly ordered doped T-(CH)$_x$. In the limit of low frequency,

$$\epsilon \simeq -\omega_p^2 \tau_{tr}^2 \left[1 - \frac{c_\perp}{2}\left(\frac{\tau_{in}(T)}{\tau_{tr}}\right)^{3/2}\right] \tag{2}$$

$$\sigma \simeq \frac{\omega_p^2 \tau_{tr}}{4\pi}\left[1 - c_\perp \sqrt{\frac{\tau_{in}(T)}{\tau_{tr}}}\right] . \tag{3}$$

While τ_{tr} in Eqs. 2 and 3 is assumed T-independent, τ_{in} increases as temperature decreases. The contribution of localization effects (second term in brackets in Eqs. 2 and 3) becomes strong and the absolute values of ϵ and σ decrease with decreasing temperature. Also, one can expect a stronger T-dependence of ϵ compared to that of σ in Eqs. 2 and 3. The metal-nonmetal transition may occur when the second term of Eq. 2 is close to unity. This analysis accounts for the observed temperature behavior of ϵ_{mw} and σ_{mw}.

Recently developed camphor-sulfonic-acid doped polyaniline cast from *m*-cresol solvent [PAN-CSA (*m*-cresol)] samples also show negative ϵ_{mw} and the existence of a maximum σ_{dc} and σ_{mw} at ~ 200 K [21]. However both ϵ_{mw} and σ_{mw} of both highly conducting stretched and unstreched doped T-(CH)$_x$ at RT are much higher than those of PAN-CSA (*m*-cresol) and yet there is no maximum in the conductivity below RT. Also, $\epsilon_{mw}(T)$ of highly conducting T-(CH)$_x$ more rapidly decreases compared to that of PAN-CSA (*m*-cresol). The estimated ω_p and τ of T-(CH)$_x$ are larger than those of PAN-CSA (*m*-cresol) sample. The differences between the two materials likely originate from the structure. While polyaniline has a relatively complicated chemical structure, consisting of C_6H_4 rings connected by NH groups (allowing low frequency ring torsional and vibrational modes), the structure of $(CH)_x$ is much simpler. Therefore there exist fewer phonons in $(CH)_x$ materials for inelastic backward scattering. As a result the region of metallic temperature behavior of σ_{dc} is absent in $(CH)_x$.

The T-dependence of $\epsilon_{mw}/\epsilon_{mw}(\mathrm{RT})$ for three differently aged I_3 doped stretched samples are compared in Fig. 3. For A1, ϵ_{mw} and σ_{mw} are measured immediately after doping. Samples A2 and A3 were kept inside a glove box (≤ 1 ppm O_2, ≤ 1 ppm H_2O) for ~24 and ~48 hours, respectively, at RT without coating after doping. The ratio of $\epsilon_{mw}/\epsilon_{mw}(\mathrm{RT})$ decreases more rapidly with decreasing temperature for increasing aging time. The $\sigma_{mw}/\sigma_{mw}(\mathrm{RT})$ of A1, A2, and A3 are similar to the dielectric response. Aging effects (from loss of dopant, redistribution of dopant, and/or the interaction of dopant with the polymer backbone) increase the localization. Hence determination of the intrinsic metallic state requires studies of freshly doped samples.

The huge negative microwave dielectric constant and the small plasma frequency $\omega_p \simeq 0.025$ eV ($\simeq 200$ cm^{-1}) determined here for heavily-doped stretched $(CH)_x$ are supported by earlier optical studies. Woo *et. al.* [22] reported a minimum in the optical conductivity at ~200 cm^{-1} which agrees with the ω_p obtained from microwave experiments. Also, Tanaka *et. al.* [23] have measured the optical dielectric constant and conductivity of stretched heavily-doped Naarmann polyacetylene [N-$(CH)_x$] samples. The frequency dependent ϵ of the doped N-$(CH)_x$ sample in the chain direction is negative and increases rapidly as the frequency is lowered below 300 cm^{-1}, in accord with the huge negative value for the dielectric constant we report for microwave frequencies. The frequency-dependent optical conductivity of Tanaka *et. al.* also show a minimum at ~200 cm^{-1}.

In sum, a huge negative ϵ_{mw} for highly conducting T-$(CH)_x$ indicates the intrinsic metallic nature of the system though with an anomalously long relaxation time compared to standard metals such as Nb. The temperature dependence of ϵ_{mw} and σ_{mw} of doped $(CH)_x$ can be understood by using a modified Drude model which takes into account the 1d weak localization effects due to inhomogeneous disorder within the fibril structure.

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FIGURES

FIG. 1. Temperature dependent microwave dielectric constant $[\epsilon_{mw}(T)]$ of center portions of six-fold stretched (solid squares) and unstretched (open squares) heavily iodine doped Tsukamoto polyacetylene. Inset: microwave dielectric constant of Nb samples as a function of temperature.

FIG. 2. Temperature dependent microwave conductivity $[\sigma_{mw}(T)]$ of center portions of six-fold stretched (solid squares) and unstretched (open squares) heavily iodine doped Tsukamoto polyacetylene. Inset: microwave conductivity of Nb samples as a function of temperature.

FIG. 3. Normalized microwave dielectric constant $[\epsilon_{mw}/\epsilon_{mw}(\mathrm{RT})]$ as a function of temperature for three differently aged samples of heavily iodine doped T-$(CH)_x$ A1, A2, and A3. See text.

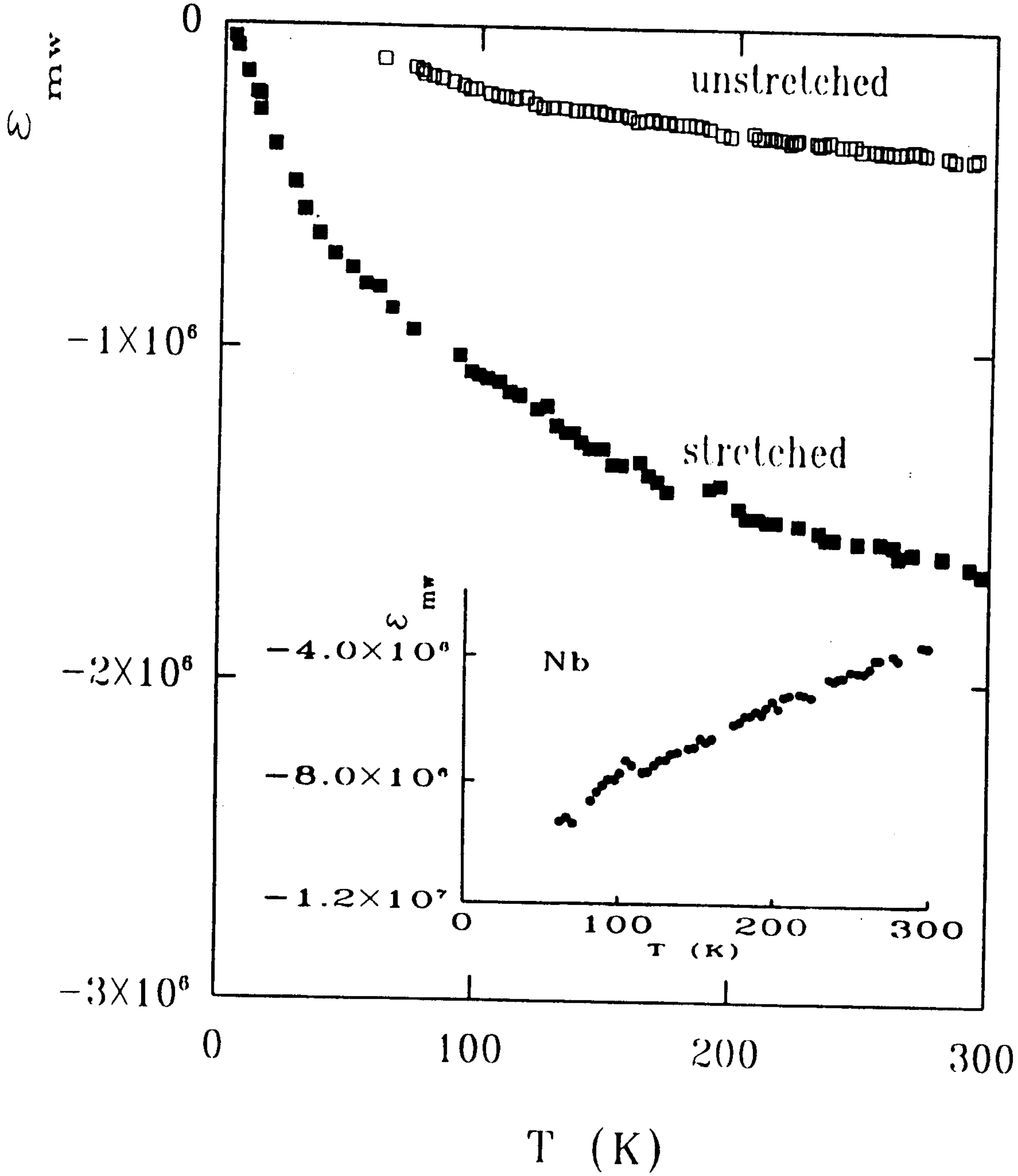

Fig. 1 Joo et. al.

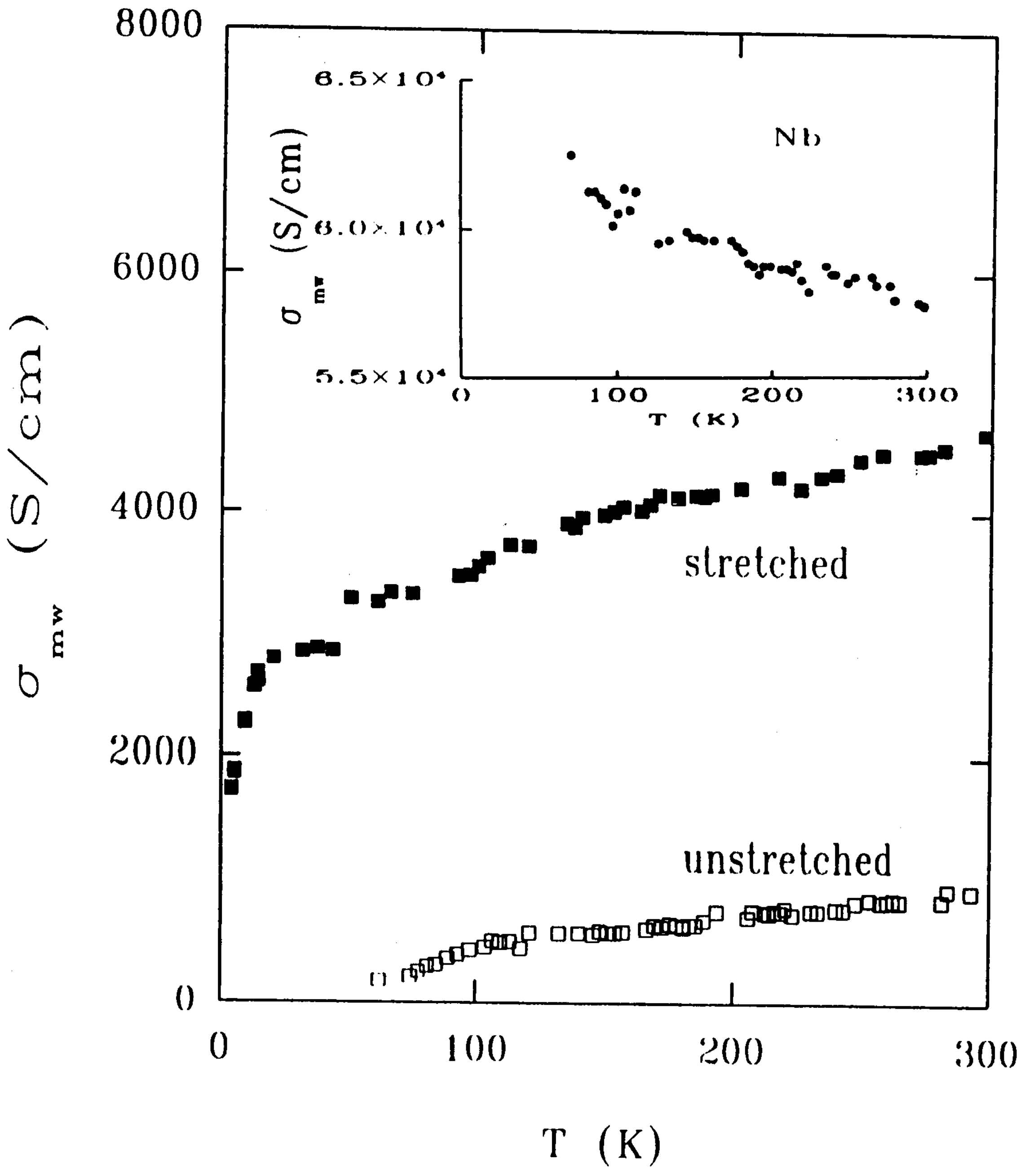

Fig. 2 Joo et.al.

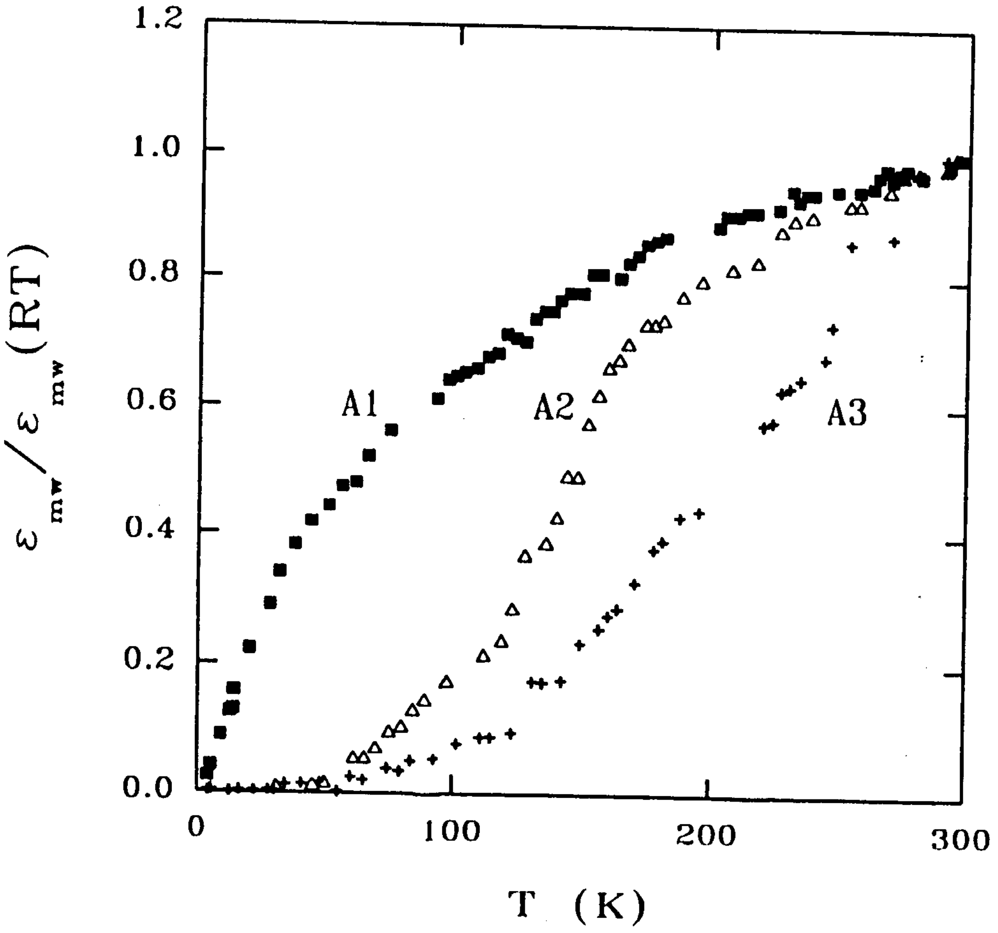

Fig.3 Juo et al.