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Charge ordering in quasi one-dimensional semiconductor $(\text{NbSe}_4)_3\text{I}$

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Abstract. We have observed surprisingly huge dielectric response in a nominally semiconducting quasi one-dimensional system $(\text{NbSe}_4)_3\text{I}$ below structural phase transition at 274 K. While the relaxation time shows activated increase on cooling almost following the increase of dc resistivity, the dielectric constant goes through a maximum at 150 K. We discuss the results in the view of charge reordering at 274 K.

1. INTRODUCTION

Quasi one-dimensional (q1D) systems exhibit a number of fascinating phenomena related to the peculiarities of the 1D physics. One such example is the family of iodine doped transition-metal tetraselenides $(\text{MSe}_4)_n\text{I}$ with $\text{M} = \text{Nb}, \text{Ta}$ and $n = 2, 3$, and $10/3$ [1, 2, 3, 4, 5]. They consist of chains of M atoms surrounded by rectangular Se antiprisms which are stabilized by I ions between the chains. The filling of metal dz^2 band which governs the electronic properties is determined by n as $(n - 1)/2n$ [3]. $(\text{TaSe}_4)_2\text{I}$, $(\text{NbSe}_4)_2\text{I}$, and $(\text{NbSe}_4)_{10/3}\text{I}$ are metallic at room temperature and undergo Peierls transitions with charge density wave (CDW) formation [6, 7, 8]. However, $(\text{NbSe}_4)_3\text{I}$ was found to be a charge-ordered semiconductor at room temperature exhibiting a displacive-like structural phase transition at $T_c = 274\text{ K}$ [9, 10] to another insulating phase not associated with CDW formation. The semiconducting nature turned out to be a consequence of the $1/3$ band filling and lattice trimerization [3], while the displacive-like transition which doubles the unit cell perpendicular to the chains has been described by the pseudo Jahn-Teller effect [10] not uncommon to narrow band semiconductors.

Naively, the formation of CDW can be viewed as a specific type of charge order (CO). In transition-metal oxides, CO is a common phenomenon which is widely investigated, so the charge-ordered state in $(\text{NbSe}_4)_3\text{I}$ received recently again some attention and indeed showed several unexpected phenomena. Unusual dynamic properties in optical spectroscopy and photoemission [11], large thermopower that changes sign at finite temperature [12] and incomplete phonon softening at T_c [13] originating from the coupling to the purely electronic order parameter are among them.

It is well known that at audio frequencies CDW systems reveal unusually large dielectric constants and strong dispersion effects as discussed in detail by Cava et al. [14, 15] and as observed also for $(\text{TaSe}_4)_2\text{I}$ and $(\text{NbSe}_4)_{10/3}\text{I}$ [16]. Hence, in CDW systems dielectric spectroscopy provides important information on CDW properties. In CO systems an increasing number of dielectric measurements close to charge-ordering transitions were reported as well, specifically in low-dimensional systems having in mind the close analogy to the Peierls transition in metallic systems. Indeed, a giant dielectric response has been detected in the insulating two-leg ladder $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ [17, 18] and in one-dimensional $(\text{DI-DCNQ})_2\text{Ag}$ [19]. Thus it seems promising to investigate also the insulating charge-ordered tetraselenide $(\text{NbSe}_4)_3\text{I}$ by broadband dielectric spectroscopy. Here we report the dielectric permittivity from sub-audio to radiowave frequencies. Below T_c we find frequency and temperature dependent dielectric constant very similar to what is observed in CDW systems [14, 15, 16], despite the fact that the phase transition in $(\text{NbSe}_4)_3\text{I}$ can not be characterized as a Peierls instability.

2. EXPERIMENTAL AND RESULTS

The broadband dielectric response from 10 mHz to 100 MHz has been determined utilizing frequency-response analysis and a reflectometric technique [20] employing the Novocontrol α -analyzer and the impedance analyzer Agilent 4294A. The dielectric constant ε has been calculated from the measured complex conductivity σ as $\varepsilon = (\sigma - \sigma_{dc}) / (i2\pi\nu)$ where ν is frequency and σ_{dc} the low frequency-independent conductivity. Measurements on several needle-shaped samples of cross-section $5 \cdot 10^{-9} - 6 \cdot 10^{-8} \text{ m}^2$ and length 0.9 – 4.5 mm were performed along the crystallographic c-direction for temperatures from 1.5 K < T < 300 K. Typical amplitude of the driving signal of 0.1 V has been verified not to induce any non-linear effects at several temperatures in the range of our experiments. The samples have also been characterized by dc resistivity, heat capacity and magnetization measurements, which will be reported separately [21]. The measurements on different samples yield quantitatively very similar results. The resistivity at room temperature is of the order 1.6 Ωcm , close to the values reported in literature [9].

Figure 1 shows the temperature dependence of the real part of the dielectric constant $\text{Re } \varepsilon$. Starting at the room temperature, the dielectric constant increases, reaches colossal values of the order of 10^5 near 150 K, and finally drops below 10^2 at low temperatures. The temperature dependence of the dielectric constant closely resembles the observations in the CDW systems $(\text{NbSe}_4)_{10/3}\text{I}$ and $(\text{TaSe}_4)_2\text{I}$. In these compounds the dielectric constant strongly increases in the Peierls state reaching values of 10^6 and smoothly decreases towards low temperatures, again revealing strong dispersion effects [16]. However, no nonlinear conductivity has been observed in the electric fields up to 100 V/cm.

The frequency dependence of the dielectric loss ($\text{Im } \varepsilon$) at selected temperatures between 60 K and 220 K is presented in Figure 2. It shows a broad peak, typical for relaxational behavior, with the mean relaxation frequency ν_0 (position of the peak) strongly shifting towards lower values with decreasing temperature. Real (not shown) and imaginary part of the dielectric constant can be consistently described with a symmetrically broadened Debye relaxation (Cole-Cole) with the width parameter for all temperatures close to 0.8.

The amplitude of the relaxation process $\Delta\varepsilon$ obtained from the fit is presented as a solid line in Figure 1 and the mean relaxation time $\tau_0 = 1/\nu_0$ in Figure 3 together with $\rho_{dc} = 1/\sigma_{dc}$ obtained from

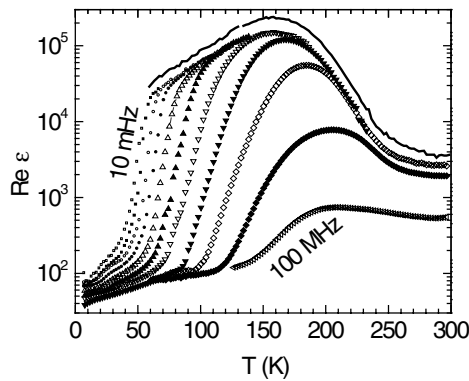


Figure 1. Temperature dependence of the dielectric constant $\text{Re } \varepsilon$ of $(\text{NbSe}_4)_3\text{I}$ for selected frequencies. The solid line represents the static susceptibility $\Delta\varepsilon$ (slightly shifted upwards) as determined from the analysis of the frequency-dependent data.

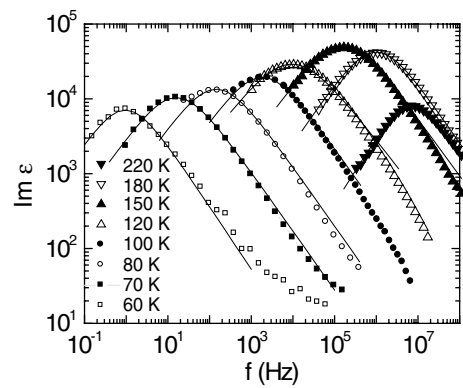


Figure 2. Frequency-dependence of the dielectric loss $\text{Im } \varepsilon$ of $(\text{NbSe}_4)_3\text{I}$ at selected temperatures. The lines are fits to the empirical Cole-Cole function.

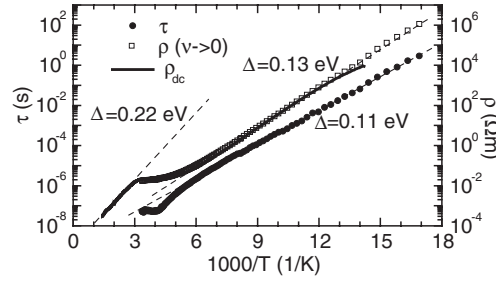


Figure 3. The relaxation time τ (circles; from an analysis of the frequency-dependent spectra in Figure 2) and the dc conductivity ρ_{dc} [solid line: 4-point dc measurement, squares: from $\sigma'(v)$] of $(\text{NbSe}_4)_3\text{I}$ in an Arrhenius representation. Dashed lines demonstrate the thermally activated behavior.

dielectric measurements and four contact dc measurements. In the Arrhenius presentation in Figure 3 the linear dependence of τ_0 between 60 K and 150 K (dashed line) exemplifies the thermally activated dipolar relaxation over an energy barrier of 0.11 eV (≈ 1300 K). This value is only slightly lower than the activation energy Δ of 0.13 eV determined from the low temperature ρ_{dc} and strongly resembles the effects of screening in the pinned CDW as explained by Littlewood [22]. The four contact $g\rho_{dc}$ has been measured up to 700 K and shows that the above the low temperature activated dependence ρ_{dc} goes actually through a “plateau” region between 250 K and 300 K with an effective Δ of only 4 meV and then decreases again in the activated manner with an increased Δ of 0.22 eV. At $T_c = 274$ K only a small kink is observed.

3. DISCUSSION AND CONCLUSION

$(\text{NbSe}_4)_3\text{I}$ is typically considered as a narrow gap semiconductor in which the gap increases below the displacive transition. However, ρ_{dc} data between 70 K and 700 K indicate that it would be reasonable to consider the region around T_c as a crossover between two activated regimes, one above 300 K and the other below 200 K. Gressier et al. have shown in [3] that the trimerized Nb chains in $(\text{NbSe}_4)_3\text{I}$ can have two stable distorted structures with a very small stability difference. In one of them (i) two Nb atoms form a dimer at which both electrons reside leaving the third Nb atoms isolated and unoccupied, while in the other (ii) all three Nb atoms in unit cell approach and share all the electrons. The Nb distance sequence of LLS (L-long, S-short) observed at room temperature [1] corresponds nicely to (i), while the complicated one deduced at 30 K [23] is actually close to LSS corresponding to (ii). The LMS (M-medium) sequence at 128 K [5] seems like some kind of intermediate, or crossover case. Moreover, the continuous change of the distorted structure from (ii) to (i) with decreasing temperature would qualitatively lead to the observed $\rho_{dc}(T)$ dependence. In this process the nodal properties of the top of the valence band and the bottom of the conducting band should reverse as well [3]. As the main feature of the displacive transition is to lift the central symmetry through the relative shift of two adjacent chains, maybe only the nodal properties are reversed at T_c creating a double well potential for the isolated Nb atom. As the temperature is decreased below T_c this atom has to approach one of the dimers leading to a ferroelectric-like distortion within one chain and the huge polarizability that we observe. In the adjacent chain, based on the relative displacement of the chains, the isolated Nb atom should displace in the opposite direction but the dipolar interaction could favor its displacement in the same direction as in the first chain. This kind of frustration might be at the origin of the pronounced dispersion resembling strongly the case of relaxor ferroelectric systems [24]. However, the relaxor behavior is observed in diluted ferroelectrics where the long-range ferroelectric order is suppressed by disorder and frustration while $(\text{NbSe}_4)_3\text{I}$ is a purely stoichiometric compound.

In conclusion, below the displacive transition temperature we observe an unexpectedly high dielectric constant in nominally semiconducting q1D system $(\text{NbSe}_4)_3\text{I}$, which also exhibits a strong dispersion at low frequencies, much alike the CDW systems of similar structure. Based on available structural data at different temperatures we propose a model that might explain both features through the competition of the interchain ferroelectric ordering favored by dipolar interactions and the intrachain antiferroelectric ordering favored by the chain displacement.

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