Volume dependent quasiparticle spectral weight in NiS$_{2-x}$Se$_x$ system.

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Abstract. We discuss the evolution of infrared reflectivity at room temperature under various pressures (P) and Se alloying concentration in the strongly correlated NiS$_{2-x}$Se$_x$ pyrite. Measurements gave a complete picture of the optical response of the system on approaching the P-induced and Se-induced metallic state. A peculiar non-monotonic (V-shaped) volume dependence was found for the quasiparticle spectral weight of both pure and Se-doped compounds.

1. Introduction
In the past sixty years, much progress has been made from both theoretical and experimental sides in understanding strongly correlated electrons and metal insulator transition (MIT)[1]. Cubic NiS$_{2-x}$Se$_x$ series provided an important model system for a systematic investigation, exhibiting a MIT controlled by varying the Se content x, or pressure P[2, 3, 4].

The two end members of the family, NiS$_2$ and NiSe$_2$, are charge transfer (CT) insulators [5] and metals[6] respectively; they can be mixed in all proportions, thereby permitting a graded variation in electrical and magnetic properties through adjustment of the stoichiometry ratio x: NiS$_{2-x}$Se$_x$ exhibits first an anti-ferromagnetic insulator ground state for zero and low Se-content and then it enters an anti-ferromagnetic metallic phase around x = 0.40. A paramagnetic metallic ground state is finally achieved at room temperature around x = 0.60 [7].

An alternative way to induce a metallic state in NiS$_2$ is applying a hydrostatic P. A P-induced MIT was observed in pure NiS$_2$ for P > 4GPa[4, 9, 10, 11]. Whereas chemical substitution inevitably introduces impurities, changing many physical parameters in an uncontrollable way, P offers a more systematic way of tuning the properties.

Infrared spectroscopy is a powerful tool to study the properties of a system since the optical response of the free-charge carriers is determined by the frequency-dependent complex

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Recently, we carried out an infrared (IR) investigation on several compounds of the NiS$_{2-x}$Se$_x$ pyrite family (i.e. $x = 0.00, 0.55, 0.60,$ and $1.20$)\[10]. In this paper, we present the new high P (HP) IR data on the $x = 0.55$ sample re-discussing the already published ones, thus obtaining a deeper insight into low energy electron dynamics in the system.

2. Experimental methods

The measurements were performed at the high brightness infrared synchrotron-radiation source SISSI@Elettra (Trieste)\[12], using a cassegrain-based Hyperion 2000 IR microscope equipped with a MCT detector and coupled to a Bruker IFS 66v interferometer. A screw clamped opposing-plate diamond-anvil cell (DAC) equipped with 800 µm culet II A diamonds has been used for IR HP experiments. Pressure has been determined by ruby fluorescence technique\[13]. Thick Sample slabs have been obtained by pressing finely milled sample powder between the diamond anvils. The sample slabs have been placed on top of a pre-sintered KBr pellet in the gasket hole\[14]. This procedure ensures a clean sample-diamond interface, where reflectivity spectra, $R_{sd}(\omega)$, have been measured. Further details on the measurement procedures are reported elsewhere\[10, 15].

3. Results and discussion

Room temperature NiS$_{2-x}$Se$_x$ reflectivity curves $R(\omega)$ were measured as a function of $x$ (i.e. $x = 0.00, 0.55, 0.60,$ and $1.20$) between 50 and 35 000 cm$^{-1}$ on well characterized high-density pellets. The $R(\omega)$ of NiS$_2$ at ambient P, shown in panel (a) of Fig. 1, is nearly flat from 50 to 10 000 cm$^{-1}$ except for weak phonon contributions at 260 and 290 cm$^{-1}$. On increasing the Se content, $R(\omega)$ is progressively enhanced at low frequencies, characteristic of a metallic behavior. $R_{sd}(\omega)$ as function of P for the pure and $x = 0.55$ compounds are shown in panel (b) and (c) respectively. Zero pressure reflectance spectrum, as previously evaluated at the diamond-sample interface\[10], is also shown for comparison. In the parent compound on increasing the pressure, $R_{sd}(\omega)$ progressively increases at low frequency showing an overdamped behavior, as a signature of a correlated bad metallic state. At high frequencies all $R_{sd}(\omega)$ converge above 10 000 cm$^{-1}$.

![Figure 1](image_url)

**Figure 1.** (a) ambient conditions $R(\omega)$ for several compounds of the NiS$_{2-x}$Se$_x$ pyrite family (i.e. $x = 0.00, 0.55, 0.60,$ and $1.20$); NiS$_2$ (b) and NiS$_{1.45}$Se$_{0.55}$ (c) $R_{sd}(\omega)$ as function of P.
On increasing P in Se-substituted sample a similar $R_{sd}(\omega)$ behavior is observed. Also in this case the progressive enhancement of the $R_{sd}(\omega)$ suggests the crossover between insulator and metallic states.

Reflectivity spectra have been analyzed through a Drude-Lorentz model with three oscillators: a Drude term, a broad mid-infrared contribution centered around 2000 cm$^{-1}$, and an intense high frequency contribution centered around 10000 cm$^{-1}$ which mimic the quasi-particle (QP) coherent excitations around the Fermi Energy and QP transitions from the QP peak to the upper and lower Hubbard bands respectively [10]. X and P effects can be thus enlightened by an analysis of the spectral weight (SW), defined as the integrated area of Drude plus mid-IR components. On increasing the Se content a linear increase of SW is observed, as shown in panel (a) of fig. 2. We turn now to the high-P measurements. For the both parent and Se substituted compound SW is nearly zero at ambient-P and then increases reflecting the progressive enhancement of the electron kinetic energy corresponding to the metallization of the system. A change of the slope is thus observed above 5 and 2 GPa respectively.

Figure 2. Quasi-particle spectral weight of NiS$_{2-x}$Se$_x$ as function of x (a) and as function of P (b) for x = 0.00 and x = 0.55 Se substituted NiS$_{2-x}$Se$_x$ pyrite.

4. Conclusions
The measurements presented here together with those reported in Ref. [10] provide data on the dependence of the quasi-particle spectral weight on pressure P and Se alloying of NiS$_{2-x}$Se$_x$ system. All the data can be plotted together by considering their dependence from the volume, bearing in mind that V is compressed by P while it is expanded by x. For the volume expansion given by Se alloying, X-ray diffraction data are available in the literature[16], while for the volume compression given by P structural data are only available for NiS$_2$ up to 6.5 GPa[17]. However, a reliable estimation of V at higher P values for NiS$_2$ and for all the pressures in Se-substituted compounds can be obtained by using the procedure previously developed in ref. [18]. Briefly, through the specific-heat data[19, 20] it is possible to estimate the bulk modulus of the system. The Murnagham Equation[21] finally provides the pressure dependence of V. This procedure gives volume values in very good agreement with those resulting from LDA calculations for NiS$_2$ up at least 10 GPa[10].
Figure 3. Quasi-particle spectral weight of NiS$_{2-x}$Se$_x$ as a function of volume: red open circles $x=0.00$, blue full circles $x=0.55$ (present data), triangles ambient condition $x=0.00$, 0.55, 0.60, and 1.20. The hatched stripe mark the volume region where the MITs occurs (see the text).

The volume dependence of SW is reported in Fig. 3. In pure NiS$_2$, SW slightly decreases on increasing V up to $\sim 173$ A$^3$, i.e. on releasing P from highest value down to $\sim 5$ GPa, and then drops to the minimum value on further increasing V up to 183 A$^3$, i.e. to the volume of NiS$_2$ at ambient P. Finally on entering the Se alloying regime (i.e. V > 183 A$^3$) the SW restarts to raise, due to the decrease of the charge transfer gap. This originates a characteristic V shape behaviour. As to $x=0.55$ compound, SW decreases more slowly on increasing the volume, with a change in slope at $\sim 183$ A$^3$ (i.e. at $\sim 2$ GPa), and reaches the minimum value around 191 A$^3$, corresponding to the volume at ambient P of NiS$_{1.45}$Se$_{0.55}$. On further increasing V a new metallization occurs (due to the charge gap closure). The main effect of Se substitution results in a less pronounced V shape behavior. This is because the p orbitals of the Se$_{2}^-$ ion have larger spatial extent than those of S$_{2}^-$ and hence larger p-d and p-p transfer interactions, resulting in a less pronounced insulating character, as also suggested by the greater SW value at zero P.

In summary, a detailed IR study on the P- and x- induced MITs in NiS$_{2-x}$Se$_x$ pyrite has been presented. A strong non monotonic behaviour of the quasiparticle SW as function of the volume is observed and discussed. Present results open to new experimental and theoretical quests aimed at addressing the effects of increasing electron-electron interaction by appropriate changes in the unit cell volume in strongly correlated system.

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