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Amplitude Higgs mode in the $2H$-$NbSe_2$ superconductor

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We report experimental evidence for the observation of the superconducting amplitude mode, the so-called "Higgs" mode, in the charge density wave superconductor $2H$-$NbSe_2$ using Raman scattering. By comparing $2H$-$NbSe_2$ and its isostructural partner $2H$-NbS_2 which shows superconductivity but lacks the charge density wave order, we demonstrate that the superconducting mode in $2H$-$NbSe_2$ owes its spectral weight to the presence of the coexisting charge density wave order. In addition, temperature dependent measurements in $2H$-$NbSe_2$ show a full spectral weight transfer from the charge density wave mode to the superconducting mode upon entering the superconducting phase. Both observations are fully consistent with a superconducting amplitude mode or Higgs mode.

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While the quest for the Higgs boson in particle physics is reaching its goal and its prediction has been rewarded by the Nobel prize, there is growing interest in the search for an analogous excitation in quantum many body systems where the Higgs boson manifests itself as a fundamental collective mode [1–3]. When a spontaneous breaking of a continuous symmetry takes place, collective excitations of the order parameter emerge: They are the massless Nambu-Goldstone phase modes [4] and the massive amplitude Higgs mode [5]. In quantum many body systems, the Higgs mode was recently identified in ultracold two-dimensional (2D) bosonic ^{87}Rb atoms in an optical lattice [6] and was reported in the dimer antiferromagnet $TlCuCl_3$ [7]. Very recently, it has been unveiled in superconducting $Nb_{1-x}Ti_xN$ films by using terahertz pump probe spectroscopy [8]. The existence of a Higgs mode was proposed more than 30 years ago in the bulk charge density wave (CDW) superconductor (SC) $2H$-$NbSe_2$ [9,10], where a superconducting amplitude mode, or Higgs mode, can be unraveled via its coupling to the coexisting charge density wave mode. Despite this prediction after the first experimental observation by Raman scattering [11,12], unambiguous proof of its Higgs type nature has remained elusive [13–15].

As it does not carry any spin or charge, in principle, the amplitude mode of the superconducting order parameter, or the Higgs mode, does not couple directly to any external probe. However, when superconductivity coexists with a charge density wave order, the amplitude mode of the CDW order couples to the Higgs mode by modulating the density of states at the Fermi level, thus "shaking" the SC condensate by modulating the amplitude of the superconducting order parameter. This allows the indirect detection of the "Higgs" mode by spectroscopic probes [9,10]. Experimentally, the Higgs mode becomes active by removing spectral weight from the CDW amplitude mode upon entering the SC state. The requisite of a coexisting CDW mode and the observation of a transfer of spectral weight from the CDW amplitude mode to the Higgs mode in the SC state can thus be considered as key predictions of the Higgs mode scenario.

Raman inelastic light scattering experiments allow access to symmetry dependent collective excitations of both CDW and SC orders. Crucially, because the amplitude mode of the CDW order is Raman active [16], it is ideally suited for the detection of the Higgs mode in the SC state. The Raman response of $2H$-$NbSe_2$ has been extensively studied [16–20], including at low temperature, in the superconducting phase [11,12]. On the contrary, $2H$-NbS_2 has been little investigated by Raman spectroscopy [21,22] and attempts to perform measurements in the superconducting state have yet to be performed. Because $2H$-NbS_2 does not show any CDW order, its comparison with $2H$-$NbSe_2$ provides a stringent test for the Higgs mode scenario.

We show here, by a comparison of quantitative Raman scattering measurements in $2H$-$NbSe_2$ and $2H$-NbS_2, that the narrow and intense superconducting mode in $2H$-$NbSe_2$ cannot be a simple Cooper-pair-breaking mode. In $2H$-NbS_2, only a much weaker Cooper-pair-breaking peak is observable. Clearly, the coexisting CDW mode is necessary for the observation of the intense superconducting mode in $2H$-$NbSe_2$. We also report an almost perfect transfer of spectral weight from the CDW mode to the SC mode from T_c down to 2 K in $2H$-$NbSe_2$ in A_{1g} and E_{2g} symmetries, showing that the SC mode draws all its Raman intensity from the coexisting CDW mode. Both experimental observations are strong evidence for the Higgs mode scenario in $2H$-$NbSe_2$.

The dichalcogenide $2H$-$NbSe_2$ offers the unique feature of exhibiting charge density wave and superconducting ordering temperatures of the same order of magnitude ($T_c = 7.1$ K and $T_{CDW} = 33$ K, respectively). This property allows an efficient coupling between the CDW mode and the amplitude mode of the SC order parameter, a prerequisite for the detection of the amplitude SC mode or Higgs mode. Whereas $2H$-$NbSe_2$ exhibits coexisting SC and CDW orders, its isostructural and isoelectronic partner $2H$-NbS_2 presents only the superconducting state with a comparable T_c

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(6.05 K). Both compounds have similar superconducting properties which have been interpreted as either multiple SC gaps or a single anisotropic SC gap [23–28]. Moreover, the Fermi surface of both compounds seems to differ only by the absence of the pancakelike sheet at the Γ point in NbS_2 [29] whereas the two cylindrical Fermi-surface sheets centered at the Γ and K points are present in both compounds [26,29,30]. Recent inelastic x-ray scattering studies have shown that $2H$-NbS_2 is on the verge of CDW order with a softening of the phonon modes along ΓM at the same wave vector than the soft mode which drives the CDW transition in $2H$-$NbSe_2$. Most probably, in $2H$-NbS_2, CDW does not occur only due to large anharmonic effects [31].

The $2H$-NbS_2 single crystal was grown using the vapor transport growth technique with a large sulfur excess [32]. It was characterized by inelastic x-ray scattering (IXS) [31], scanning tunneling microscopy (STM) [23], specific heat [24], and penetration depth [25] measurements. All measurements indicate a high quality of this single crystal, with a sharp superconducting transition measured by specific heat of $0.05T_c$. The $2H$-$NbSe_2$ single crystal was synthesized using an iodine-vapor transport method. It has a residual resistivity ratio of 39 and the transition to the charge density wave order is clearly visible at 33 K by resistivity measurements, confirming its good quality.

A Raman scattering investigation has been carried out at low temperature down to 2 K. Single crystals of $2H$-$NbSe_2$ and $2H$-NbS_2, freshly cleaved, were cooled down in a ^{4}He pumped cryostat during the same experiment to be able to quantitatively compare the intensity of the Raman signals. The samples were kept in ^{4}He exchange gas, allowing reduced laser heating [33]. The reported temperatures include the laser heating. We have taken special care to avoid and check that the samples were not immersed in ^{4}He liquid, to avoid the Raman signature of superfluid ^{4}He at 13 cm^{-1}.

Raman scattering measurements have been performed in a quasibackscattering geometry with a triple spectrometer Jobin Yvon T64000 equipped with a liquid-nitrogen-cooled CCD detector. We have used the 514 nm excitation line from a Ar^+-Kr^+ mixed gas laser. The polarizations for the incoming and outgoing light are in the (ab) plane of the sample. In the 2H-dichalcogenides, four Raman active symmetries are expected, one A_{1g}, one E_{1g}, and two E_{2g}. In our configuration [$\vec{E} \in (ab)$], we detect the A_{1g} and the two E_{2g}. In parallel and crossed polarizations we select the $A_{1g} + E_{2g}$ and the E_{2g} modes, respectively. By scaling the E_{2g} phonon mode at about 250 cm^{-1}, the A_{1g} pure symmetry scattering is deduced by the subtraction of the E_{2g} signal from the $A_{1g} + E_{2g}$ signal.

Figure 1 shows the Raman spectra in the superconducting state, at 2 K, and just above T_c in $2H$-$NbSe_2$ and $2H$-NbS_2 and in the $A_{1g} + E_{2g}$ symmetry channel. In $NbSe_2$, the peak at ∼40 cm^{-1}, labeled the CDW mode, has been attributed to the amplitude mode of the CDW order [16]. A narrow and intense peak at ∼19 cm^{-1}, labeled the SC mode, develops below T_c, thus clearly relating its origin to the superconducting state [11,12]. Both modes are present in the A_{1g} and the E_{2g} symmetry channels. As shown in the inset of Fig. 1, in NbS_2, a small peak develops below T_c at 14 cm^{-1}. Contrary to the SC mode in $NbSe_2$, it is broad, spreading up to 30 cm^{-1}. Its

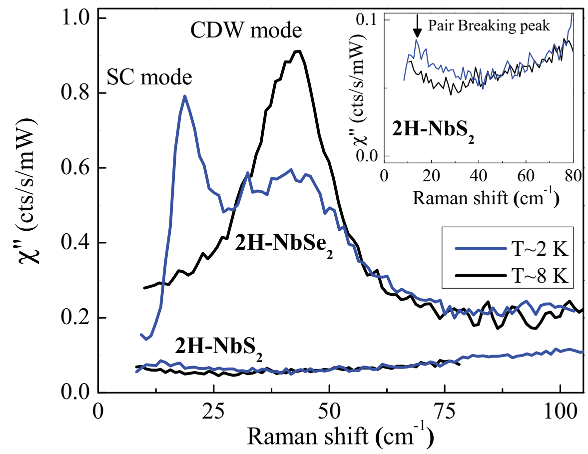

FIG. 1. (Color online) Quantitative Raman susceptibility for $2H$-$NbSe_2$ and $2H$-NbS_2 just above T_c and below T_c at 2 K in $A_{1g} + E_{2g}$ symmetry. SC mode: Amplitude mode or "Higgs" mode of the superconducting state of $2H$-$NbSe_2$. CDW mode: Amplitude mode of the charge density wave order of $2H$-$NbSe_2$. The inset is a zoom on the superconducting Cooper-pair-breaking peak in NbS_2. It is much less intense than the SC mode in $NbSe_2$.

energy matches the largest SC gap measured by STM [23]. In this compound with a single electronic SC order, it is most likely due to a Cooper-pair-breaking excitation [34–37].

By comparing the quantitative Raman signals, it is clear that the intensities of both SC excitations differ drastically. By subtracting the background obtained just above T_c, the Cooper-pair-breaking excitation in NbS_2 is more than 20 times smaller than the SC mode in $NbSe_2$. We conclude that the intense and narrow SC mode in $NbSe_2$ owes its Raman intensity to the presence of the coexisting CDW order. The huge difference between the intensity of the SC mode in the two compounds clearly demonstrates that in $NbSe_2$, the SC mode cannot be a simple Cooper-pair-breaking peak as in NbS_2. On the other hand, our observation is fully consistent with the Higgs mode scenario [10] whereby, in $NbSe_2$, the SC amplitude mode, or Higgs mode, is activated via its coupling to the CDW amplitude mode. In this scheme, the absence of CDW order in NbS_2 makes the Higgs mode unobservable, leaving only a much weaker Cooper-pair-breaking peak, as observed experimentally.

Additional evidence for the Higgs mode scenario can be obtained from the temperature dependence of the SC and CDW modes of $NbSe_2$. Figure 2 displays the Raman response of the electronic modes at various temperatures from 2 K up to 8 K above T_c and in $A_{1g} + E_{2g}$ and E_{2g} symmetry channels. At 2 K, the SC modes are at 18.8 ± 0.5 and 16.2 ± 0.5 cm^{-1} in $A_{1g} + E_{2g}$ and E_{2g} symmetry, respectively; it is extracted to be at 19.2 ± 0.5 cm^{-1} in A_{1g} symmetry, consistent with Sooryakumar *et al.* [11]. The SC mode softens with increasing temperature whereas the position of the CDW mode stays almost constant in $A_{1g} + E_{2g}$ symmetry and slightly shifts to lower energy (∼3 cm^{-1}) in E_{2g} symmetry. Crucially, the SC and CDW modes develop in an opposite way: When superconductivity is gradually destroyed, the SC mode intensity collapses while the CDW mode intensity recovers. A quantitative analysis of the spectral weight transfer as a

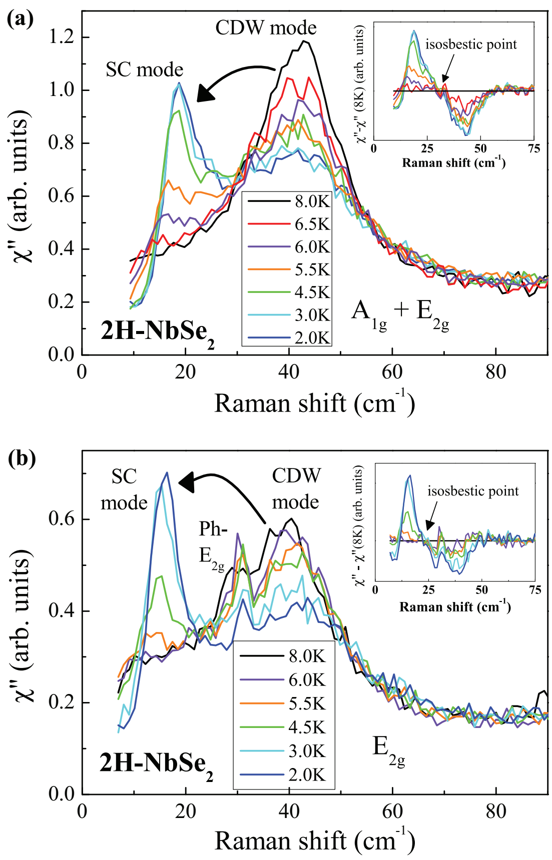

FIG. 2. (Color online) Temperature dependence of the Raman susceptibility of the charge density wave mode and the superconducting mode in 2*H*-NbSe$_2$. (a) In the $A_{1g} + E_{2g}$ symmetry. (b) In the E_{2g} symmetry. Ph-E_{2g} is the interlayer phonon mode. The black arrows depict the spectral weight transfer from the CDW mode to the SC mode upon entering the SC state. The insets show the Raman spectra subtracted from the one measured at 8 K above T_c and the arrows point to the isosbestic points, at 29 and 24 cm^{-1} in the $A_{1g} + E_{2g}$ and the E_{2g} symmetries, respectively.

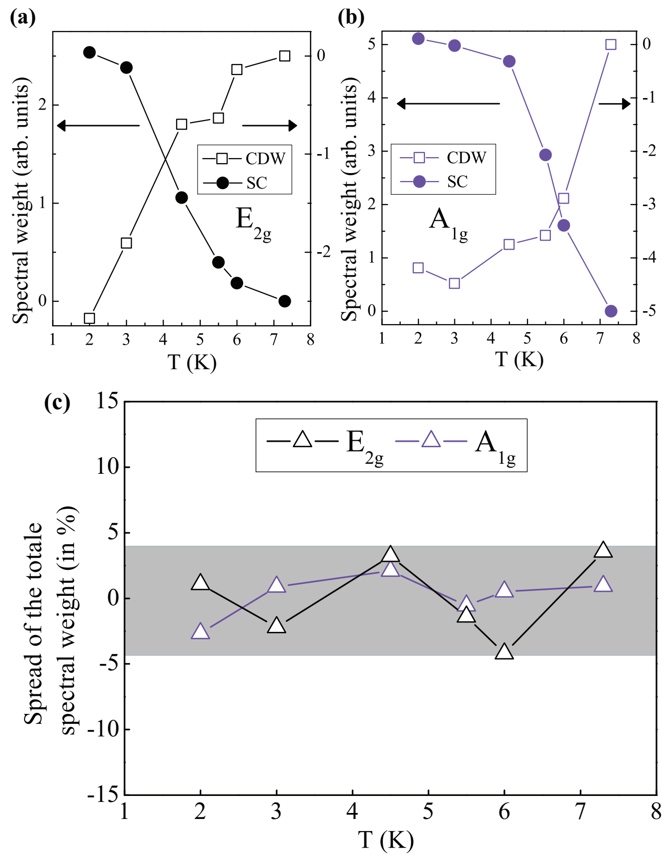

FIG. 3. (Color online) (a) and (b) Spectral weight of the SC and CDW modes of 2*H*-NbSe$_2$ vs temperature, calculated on the subtracted data (cf. the insets of Fig. 2) from 8 cm^{-1} up to the isosbestic point and from the isosbestic point up to 60 cm^{-1} for the SC and the CDW modes, respectively. (a) E_{2g} symmetry. (b) A_{1g} symmetry. (c) Percentage of spread of the total spectral weight (CDW mode+SC mode) calculated between 8 and 60 cm^{-1} in E_{2g} and A_{1g} symmetries vs temperature.

function of temperature in both A_{1g} and E_{2g} symmetries is displayed in Fig. 3. The pure A_{1g} symmetry response is shown in the Supplemental Material [38]. The spectral weight is obtained by integrating the imaginary part of the susceptibility $S = \int_{\omega_1}^{\omega_2} \chi''(\omega)d\omega$. The spread of the spectral weight is defined as the deviation from the average value $\langle S\rangle$, i.e., $\frac{S-\langle S\rangle}{\langle S\rangle}$. $\langle S\rangle$ is defined as the average on the seven measured spectra (see Fig. 2). The isosbestic point is a phenomenological definition of the energy where all the spectra intersect each other. As shown in Figs. 3(a) and 3(b), in both symmetries, the spectral weights of the CDW mode and the SC mode evolve in opposite ways with temperature. While the spectral weight is transferred at a noticeably faster rate in A_{1g} symmetry than in E_{2g} symmetry below T_c, in both symmetries the total spectral weight of the cumulative modes is almost constant, with a spread of only ±4%, as reported in Fig. 3(c).

The almost perfect transfer of spectral weight from the CDW mode to the SC mode below T_c is strong evidence that the SC mode draws all its Raman intensity from the coexisting CDW mode, in full agreement with the Higgs mode scenario.

We note here that a similar transfer of spectral weight was observed by Sooryakumar *et al.* [11,12] upon applying a magnetic field. They calculated the total spectral weight in the A_{1g} symmetry as $S = \int_{\omega_1}^{\omega_2} \chi''(\omega)\omega\, d\omega$ and found it to be constant to within ±7%. In our case, however, the SC and CDW orders are tuned using temperature, without any ambiguous consideration due to the physics of the vortex with spatially varying SC order parameter. It should also be emphasized that our spectral weight transfer is observed in both A_{1g} and E_{2g} symmetries and that it is calculated as $S = \int_{\omega_1}^{\omega_2} \chi''(\omega)d\omega$, which is the one expected to be preserved in the Higgs mode scenario [10].

There are still aspects of our experimental results which deserve further scrutiny. In particular, our results show a symmetry dependence of the "Higgs" mode energies and widths, as well as symmetry dependent spectral weight transfer upon entering the SC state. Such symmetry dependence certainly deserves further theoretical investigation, by including the $\vec{k}$-space distribution of the energy of the SC gap [39] and/or the symmetry dependence of the coupling strength. Generally, even if the SC amplitude mode has a full A_{1g} symmetry (for s-wave superconductors), there is no discrepancy for its experimental observation in the higher irreducible representation E_{2g} [40].

The observation of the Higgs mode in bulk superconductors may not be the prerogative for 2*H*-$NbSe_2$. Indeed, in the *A*15 family, Nb_3Sn and V_3Si present a particularly intense and narrow SC mode in the E_g symmetry [41,42]. In both compounds, this SC mode seems coupled to the phonon mode of the same symmetry. Particularly, in Nb_3Sn, the spectral weight of the SC mode and the E_g phonon mode is constant at ±3%, reminiscent of our results on $NbSe_2$. Interestingly, in Nb_3Sn, the pure pair-breaking effect occurs in the A_{1g} symmetry, without any spectral weight transfer from a phonon as expected. Even if not pointed out at that time, it is likely that a similar mechanism as in 2*H*-$NbSe_2$ is at play in these *A*15 compounds. We note that, in V_3Si, it is surprising that such large spectral weight transfer occurs whereas the ratio between the E_g phonon mode energy ($\sim$280 cm^{-1}) and the SC mode energy ($\sim$40 cm^{-1}) is large, in contradiction with the theoretical prediction [9]. The fact that the SC modes were not observed in the samples without a martensitic transition, the proximity of the superconducting and martensitic transitions in V_3Si, the implication of the E_g mode in the tetragonal distortion [43] might point to the martensitic instability as an essential ingredient for the observation of the Higgs mode.

In conclusion, we have reported a Raman scattering investigation of the superconducting mode of the charge density wave superconductor 2*H*-$NbSe_2$. By comparing 2*H*-$NbSe_2$ with its SC partner 2*H*-NbS_2 which lacks the CDW order, we have shown that the coexisting CDW mode is a requisite to the observation of the SC mode. 2*H*-NbS_2 exhibits only a weak Cooper-pair-breaking peak. In addition, we have precisely measured the spectral weight transfer from the amplitude mode of the CDW to the SC mode in 2*H*-$NbSe_2$ with decreasing temperature and in both A_{1g} and E_{2g} symmetries. The SC mode draws all its Raman intensity from the coexisting CDW mode. Our experimental findings are fully consistent with the scenario of a SC amplitude mode of "Higgs" type. Additional evidence might come from the pressure dependency of the SC and the CDW modes with a continuous change of their coupling.

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