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Effect of non-magnetic impurities on the observation of superconducting gap excitations by Raman scattering*

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Abstract. The effect of small concentrations of non-magnetic substitutional impurities (characterized by changes in mass, nearest neighbour force constants and local electron-phonon interaction) on the observability of superconducting (SC) gap excitations in 2H-$NbSe_2$ by Raman scattering is considered within the theoretical framework of Balseiro and Falicov (BF). The phonon self-energy when evaluated for $q = 0$ using the Einstein oscillator model for the host phonons is seen to have a pole corresponding to the impurity mode besides the gap excitation one around 2Δ previously obtained by BF. A splitting of the impurity mode into two in the SC state is predicted. An enhancement occurs in the strength of the SC gap excitation peak whenever it is close to the impurity mode. The data from the experiments of Sooryakumar, Klein and Frindt on impure samples of 2H-$NbSe_2$ are discussed in the light of the present calculation.

Keywords. Non-magnetic impurities; superconducting gap excitation, charge density wave; Raman scattering; layered compounds.

1. Introduction

Recently Sooryakumar and Klein (SK) (1980) observed for the first time the superconducting gap excitations by Raman scattering in the layered compound 2H-$NbSe_2$. In the normal phase at room temperature this material shows two Raman active phonons at 234 and 248 cm^{-1}. On cooling the system below the charge density wave (CDW) transition temperature of 33°K new Raman lines appear around the low frequency of 40 cm^{-1}, which has been identified as the CDW amplitude modes, (CDW-AM). 2H-$NbSe_2$ is known to be a superconductor below 7·2°K. In the superconducting (SC) phase at 2°K, SK succeeded in observing still more Raman peaks at 18 cm^{-1} and 15 cm^{-1}, whose weighted average is approximately 16 cm^{-1}; which is close to twice the measured superconducting energy gap ($2\Delta = 17{\cdot}2$ cm^{-1}) (Clayman and Frindt 1971). SK further demonstrated that on application of a small magnetic field the strength of the latter peak reduces and gets transferred to the original CDW-AM phonon, and as the field increases to one third the critical value ($H_c = 42$ KG) the new Raman mode is totally suppressed (Sooryakumar and Klein 1981). This led them to the conclusion that the new mode is associated with superconducting gap excitations, which become observable, through their coupling to the CDW-AM phonon. The later assertion is further substantiated by the fact that ex-

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periments with samples containing non-magnetic impurities (which tend to inhibit CDW formation) do not show the new peak in the Raman spectrum (Sooryakumar *et al* 1981). This indicates that the presence of a low lying CDW phonon with energy comparable to 2Δ is crucial to the observation of the new Raman line.

Two microscopic theories have been proposed to explain this observation. The first was due to Balseiro and Falicov (BF) (1980), who interpreted the experimental results as purely a phonon self-energy effect arising from the interaction between the CDW-AM phonon and the superconducting electrons. They start with the normal electron-phonon interaction and evaluate the phonon self-energy in the $q \to 0$ limit using the BCS Hamiltonian for the superconducting electrons. This results in a pole at an energy around 2Δ, in the phonon self-energy, which is identified with the observed new mode. The second and more recent calculation was due to Littlewood and Varma (LV) (1981) which also gives results similar to the earlier one, even though the formalism is somewhat different. They argue that the vibrations of the CDW-AM phonon produce a variation in the electron density of states at the Fermi level, which in turn changes the superconducting energy gap Δ. This provides a mechanism for the interaction where the $q \to 0$ phonon decays into two electrons or two holes of opposite spin. They also include the appropriate vertex corrections due to Coulomb interaction in the phonon self-energy calculation, to ensure gauge invariance of the theory; and argue that the BF theory when made gauge-invariant would produce new modes only around the plasma frequency, which might be irrelevant to the discussion of the present SK experiment.

The aim of the present paper is to investigate the effect of non-magnetic impurities on the observation of the superconducting gap excitations by Raman scattering. It is well known that non-magnetic impurities, when present beyond a certain concentration tend to inhibit CDW formation, while having no effect on the SC transition. However, sufficiently low concentrations of these impurities, while not completely suppressing the CDW state and hence the CDW-AM modes may give rise to additional impurity phonon modes, with frequencies higher (local modes) or lower than that of the CDW-AM mode. These impurity modes in turn would couple to the SC gap excitations and to the CDW peak in various ways and consequently affect the entire Raman spectrum of the system. It is also quite likely that in the case of a normal impure superconductor (without the CDW state) the presence of an impurity mode with frequency comparable to 2Δ might render the SC gap excitations observable through Raman scattering.

Since the theories of both BF and LV give similar qualitative results we adopt the simpler BF model for the present calculation. The question of gauge invariance and its consequences are presently under investigation and will be reported separately. The presence of substitutional non-magnetic impurities will mainly perturb the lattice vibrations as well as the electron-phonon interaction locally, the effect of both of which has been incorporated here in a generalized BF framework.

In § 2, we formulate the problem and deduce expressions for the phonon self-energy. The impurities are assumed to perturb the phonon spectrum through changes in mass and nearest neighbour force constants; this has been considered in § 2.1. Section 2.2 is devoted to the case where the impurities are characterized as isotope defects, but bring about local modification in the electron-phonon interaction.

For both these cases the phonon self-energy is calculated by evaluating the elec-

tron response function in the limit $q \to 0$ (§ 2·3) assuming the Einstein model for the host phonons (§ 2.4). Section 3 deals with the detailed analysis of the results and the discussion of its pertinence to the experimental data on 2H-$NbSe_2$. A summary of the essential results and the concluding remarks are given in § 4.

2. Theory

The simple theory due to Balseiro and Falicov (1980) does not explicitly take into account the CDW formation; instead it assumes the presence of the $q = 0$, CDW-AM phonon, which, through its coupling to the superconducting electrons, gives rise to the new mode due to the SC gap excitations. Even though non-magnetic charged impurities are known to pin down the CDW and hence suppress its formation, we shall not consider this effect in the present paper. In what follows we generalize the BF model, to take into account the effect of a small concentration of randomly-substituted non-magnetic (uncharged) impurities in the system. This consists of a change in (i) the mass of the atom (ii) the nearest neighbour force constants and (iii) the local electron-phonon interaction at the impurity site. The Hamiltonian of such a system can be written as

$$H = H_{\mathrm{BF}} + H_I, \tag{1}$$

where

$$H_{\mathrm{BF}} = H_{\mathrm{BCS}} + H_p + H_{e\text{-}p}, \tag{2}$$

$$H_{\mathrm{BCS}} = \sum_{k,\sigma} \epsilon_k C^\dagger_{k\sigma} C_{k\sigma} - \Delta \sum_k (C^\dagger_{k\uparrow} C^\dagger_{-k\downarrow} + C_{-k\downarrow} C_{k\uparrow}) \tag{3}$$

being the mean field BCS Hamiltonian for the SC state. $C^\dagger_{k\sigma}$ ($C_{k\sigma}$) is the creation (annihilation) operator for an electron with wave vector k and spin σ, ϵ_k is the electronic band energy and Δ is the SC energy gap. The phonon Hamilotnian H_p is

$$H_p = \sum_q \omega_q b^\dagger_q b_q, \tag{4}$$

ω_q being the phonon frequency with wave vector q, and $b^\dagger_q$ (b_q) the phonon creation (annihilation) operators. The electron-phonon interaction term is given by

$$H_{e\text{-}p} = g \sum_{q,k,\sigma} C^\dagger_{k+q,\sigma} C_{k\sigma} (b_q + b^\dagger_{-q}). \tag{5}$$

The coupling constant g for simplicity is assumed to be independent of momentum. The contribution of the impurities to the Hamiltonian is given by

$$H_I = \sum_{i=1}^{n} \sum_{q,q'} (\lambda U^i(q,q') B_q B_{q'} + \tau V^i(q,q') A_q A_{q'}) + \alpha \sum_{i=1}^{n} \sum_{k,k',q\sigma} W^i(k,k',q) C^\dagger_{k'\sigma} C_{k\sigma} A_q, \tag{6}$$

where $$A_q = b_q + b^{\dagger}_{-q}, \tag{7a}$$

$$B_q = b_q - b^{\dagger}_{-q}, \tag{7b}$$

the mass and force constant change parameters λ and τ respectively are

$$\lambda = (M_I - M)/M_I, \tag{8a}$$

$$\tau = (\Phi - \Phi_0)/\Phi_0, \tag{8b}$$

M_I (M) being the impurity (host) mass and Φ (Φ_0) being the nearest neighbour force constant at an impurity (host) site; and α is a small change in the electron-phonon coupling constant brought about by the introduction of the impurity. Following Behera and Tripathi (1974) the kernels U and V are assumed to be of the same form and are given by

$$U^i(q, q') = u^i(q)\, u^i(q') = (4N)^{-1} (\omega_q\, \omega_{q'})^{1/2} \exp[i(q + q') \cdot R_i] \tag{9a}$$

$$V^i(q, q') = v^i(q)\, v^i(q'). \tag{9b}$$

Finally $$W^i(k, k', q) = N^{-1} \exp[i(k - k' + q)]\, R_i, \tag{9c}$$

Where R_i denotes the position of the ith impurity.

We shall evaluate the phonon self-energy for this system, by the double time Green's function technique (Zubarev 1960) using the equation of motion method. The phonon Green's function is defined as

$$\begin{aligned} D_{qq'}(t, t') &\equiv \langle\langle A_q(t), A_{q'}(t')\rangle\rangle \\ &= -i\theta(t - t') \langle [A_q(t), A_{q'}(t')]_- \rangle \end{aligned} \tag{10}$$

where $\theta(t)$ is the usual step function and $\langle \ldots . \rangle$ denotes the thermodynamic averaging. As mentioned in § 1 this Green's function will be evaluated for two different cases by considering firstly the terms involving λ and τ and secondly those with λ and α in H_I given by equation (6).

2.1 *Case I : Impurities characterized by λ and τ*

In this case the equation of motion for the Green's function (equation (10)), when Fourier transformed becomes

$$\begin{aligned} D_{qq'}(\omega) = D^0_q(\omega) \left[\delta_{-qq'} - \frac{4\lambda}{\omega_q} \sum_{i=1}^{n} u^i(-q, -q')\right] + 2\pi g\, D^0_q(\omega)\, \Gamma_{qq'}(\omega) \\ - \frac{4\pi\lambda}{\omega_q} D^0_q(\omega) \sum_{i=1}^{n} u^i(-q)\, X^i_{q'}(\omega) + 4\pi\tau\, D^0_q(\omega) \sum_{i=1}^{n} v^i(-q)\, Z^i_{q'}(\omega) \\ - \frac{4\pi\, a\lambda\tau}{\omega_q} D^0_q(\omega) \sum_{i=1}^{n} u^i(-q)\, Z^i_{q'}(\omega) - \frac{8\pi\lambda g}{\omega_q} D^0_q(\omega) \sum_{i=1}^{n} u^i(-q)\, \phi^i_{q'}(\omega), \end{aligned} \tag{11}$$

where $$a = 4 \sum_q u^i(q)\, v^i(-q), \tag{12a}$$

$$X^i_{q'}(\omega) = \sum_q u^i(q)\, \omega_q\, D_{qq'}(\omega), \tag{12b}$$

$$Z^i_{q'}(\omega) = \sum_q v^i(q)\, D_{qq'}(\omega), \tag{12c}$$

$$\Gamma_{qq'}(\omega) = \sum_{k\sigma} \langle\langle C^\dagger_{k-q\sigma}\, C_{k\sigma};\, A_{q'}(t')\rangle\rangle_\omega, \tag{12d}$$

$$\phi^i_{q'}(\omega) = \sum_q u^i(q)\, \Gamma_{qq'}(\omega), \tag{12e}$$

and the free phonon Green's function is given by

$$D^0_q(\omega) = \omega_q/\pi\,(\omega^2 - \omega_q^2). \tag{12f}$$

It is clear from (11) that in the absence of the impurities, the only term that contributes to the phonon self-energy is the second one, which involves the higher order mixed Green's function $\Gamma_{qq'}(\omega)$. The latter can be evaluated by writing its equation of motion with respect to t', which when fourier transformed is given by

$$\begin{aligned}\Gamma_{qq'}(\omega) = {} & 2\pi g\, D^0_{q'}(\omega)\, \chi_{qq'}(\omega) - \frac{4\pi\lambda}{\omega_{q'}} D^0_{q'}(\omega) \sum_{i=1}^{n} u^i(-q')\, \bar{X}^i_q(\omega) \\ & + 4\pi\tau\, D^0_{q'}(\omega) \sum_{i=1}^{n} v^i(-q')\, \bar{Z}^i_q(\omega) \\ & - \frac{4\pi a\lambda}{\omega_{q'}} \tau\, D^0_{q'}(\omega) \sum_{i=1}^{n} u^i(-q')\, \bar{Z}^i_q(\omega) \\ & - \frac{8\pi\lambda g}{\omega_{q'}} D^0_{q'}(\omega) \sum_{i=1}^{n} u^i(-q')\, \bar{\phi}^i_q(\omega),\end{aligned} \tag{13}$$

where $$\chi_{qq'}(\omega) = \sum_{\substack{k\sigma \\ k'\sigma'}} \langle\langle C^\dagger_{k-q\sigma}\, C_{k\sigma};\, C^\dagger_{k'-q'\sigma'}\, C_{k'\sigma'}(t')\rangle\rangle_\omega, \tag{14}$$

and the barred quantities $\bar{X}$, $\bar{Z}$ and $\bar{\phi}$ have similar expressions (equation 2(b) – (e)) as X, Z and ϕ with $D_{qq'}$ and $\Gamma_{qq'}$ replaced respectively by $\Gamma_{qq'}$ and $\chi_{qq'}$. While solving (11) for $X_{q'}(\omega)$ and $Z_{q'}(\omega)$ we obtain the following coupled equations

$$D(\omega)\, X^i_{q'}(\omega) - D_1(\omega)\, Z^i_{q'}(\omega) = P^i_{q'}(\omega), \tag{15a}$$

$$D_2(\omega)\, X^i_{q'}(\omega) + D_3(\omega)\, Z^i_{q'}(\omega) = Q^i_{q'}(\omega), \tag{15b}$$

whose solutions are given by

$$X^i_{q'}(\omega) = D_4^{-1}(\omega)\,[D_1(\omega)\, Q^i_{q'}(\omega) + D_3(\omega)\, P^i_{q'}(\omega)], \tag{16a}$$

$$Z^i_{q'}(\omega) = D_4^{-1}(\omega)\,[D(\omega)\, Q^i_{q'}(\omega) - D_2(\omega)\, P^i_{q'}(\omega)], \tag{16b}$$

where
$$D(\omega) = 1 + \pi\lambda\, D_{00}(\omega), \tag{17a}$$

$$D_1(\omega) = \tau\,[\pi\, D_{01}(\omega) + a\,(1 - D(\omega))], \tag{17b}$$

$$D_2(\omega) = \pi\,\lambda\, D_{02}(\omega), \tag{17c}$$

$$D_3(\omega) = 1 - \pi\,\tau\, D_{03}(\omega) + a\,\tau\, D_2(\omega), \tag{17d}$$

$$D_4(\omega) = D(\omega)\, D_3(\omega) + D_1(\omega)\, D_2(\omega), \tag{17e}$$

$$D_{00}(\omega) = 4 \sum_q u^i(q)\, u^i(-q)\, D^0_q(\omega), \tag{17f}$$

$$D_{01}(\omega) = 4 \sum_q u^i(q)\, v^i(-q)\, \omega_q\, D^0_q(\omega), \tag{17g}$$

$$D_{02}(\omega) = 4 \sum_q v^i(q)\, u^i(-q)\, \omega_q^{-1}\, D^0_q(\omega), \tag{17h}$$

$$D_{03}(\omega) = 4 \sum_q v^i(q)\, v^i(-q)\, D^0_q(\omega), \tag{17i}$$

$$P^i_{q'}(\omega) = u^i(-q')\, \omega_{q'}\, D^0_{q'}(\omega) + 2\pi\, g\, N^i_{q'}(\omega) - \lambda\, D_{00}(\omega)\,[u^i(-q') + 2\pi\, g\, \phi^i_{q'}(\omega)] \tag{17j}$$

$$Q^i_{q'}(\omega) = v^i(-q')\, D^0_{q'}(\omega) + 2\pi\, g\, M^i_{q'}(\omega) - \lambda\, D_{02}(\omega)\,[u^i(-q) + 2\pi\, g\, \phi^i_{q'}(\omega)] \tag{17k}$$

$$N^i_{q'}(\omega) = \sum_q u^i(q)\, \omega_q\, D^0_q(\omega)\, \Gamma_{qq'}(\omega) \tag{17l}$$

and
$$M^i_{q'}(\omega) = \sum_q v^i(q)\, D^0_q(\omega)\, \Gamma_{qq'}(\omega). \tag{17m}$$

Similarly the solutions for $\bar{X}_q^i(\omega)$ and $\bar{Z}_q^i(\omega)$ obtained from equation (13) are

$$\bar{X}_q^i(\omega) = D_4^{-1}(\omega)\,[D_1(\omega)\,\bar{Q}_q^i(\omega) + D_3(\omega)\,\bar{P}_q^i(\omega)] \tag{18a}$$

$$\bar{Z}_q^i(\omega) = D_4^{-1}(\omega)\,[D(\omega)\,\bar{Q}_q^i(\omega) - D_2(\omega)\,\bar{P}_q^i(\omega)] \tag{18b}$$

where
$$\bar{P}_q^i(\omega) = 2\pi g\,(\bar{N}_q^i(\omega) - \lambda D_{00}(\omega)\,\bar{\phi}_q^i(\omega)), \tag{19a}$$

$$\bar{Q}_q^i(\omega) = 2\pi g\,(\bar{M}_q^i(\omega) - \lambda D_{02}(\omega)\,\bar{\phi}_q^i(\omega)), \tag{19b}$$

and the expression for $\bar{N}$, $\bar{M}$ is similar to that for N, M (equations (17l), (17m)) with Γ replaced by χ. Substituting (16) into (11) and (18) into (13) we get

$$D_{qq'}(\omega) = D_q^0(\omega)\left[\delta_{-qq'} - \frac{4\lambda}{\omega_q}\sum_{i=1}^{n} U^i(-q,-q')\right] + 2\pi g\,D_q^0(\omega)\,\Gamma_{qq'}(\omega)$$

$$- 4\pi\lambda\,\omega_q^{-1}\,D_q^0(\omega)\sum_{i=1}^{n} u^i(-q)\,[2g\phi_{q'}^i(\omega) + D_4^{-1}(\omega)\,P_{q'}^i(\omega)]$$

$$+ \frac{4\pi\tau\,D_q^0(\omega)}{D_4(\omega)}\left\{\sum_{i=1}^{n} v^i(-q)\,[D(\omega)\,Q_{q'}^i(\omega) - D_2(\omega)\,P_{q'}^i(\omega)]\right.$$

$$\left. + \lambda\omega_q^{-1}\sum_{i=1}^{n} u^i(-q)\,[\pi D_{03}(\omega)\,P_{q'}^i(\omega) - (a + \pi D_{01}(\omega))\,Q_{q'}^i(\omega)]\right\}, \tag{20}$$

and
$$\Gamma_{qq'}(\omega) = 2\pi g\,D_{q'}^0(\omega)\,\chi_{qq'}(\omega) - \frac{4\pi\lambda}{\omega_q}\,D_{q'}^0(\omega)\sum_{i=1}^{n} u^i(-q')\,[2g\,\bar{\phi}_q^i(\omega)$$

$$+ D_4^{-1}(\omega)\,\bar{P}_q^i(\omega)] + \frac{4\pi\tau}{D_4(\omega)}\,D_{q'}^0(\omega)\left\{\sum_{i=1}^{n} v^i(-q')\,[D(\omega)\,\bar{Q}_q^i(\omega)\right.$$

$$- D_2(\omega)\,\bar{P}_q^i(\omega)] + \lambda\omega_{q'}^{-1}\sum_{i=1}^{n} u^i(-q')\,[\pi D_{02}(\omega)\,\bar{P}_q^i(\omega)$$

$$\left. - (a + \pi D_{01}(\omega))\,\bar{Q}_q^i(\omega)]\right\}. \tag{21}$$

It is clear from (21) and the definitions of the barred quantities $\bar{\phi}$, $\bar{P}$ and $\bar{Q}$ that $\Gamma_{qq'}(\omega)$ and hence the phonon Green's function $D_{qq'}(\omega)$ can be expressed in terms of the electron response function $\chi_{qq'}(\omega)$. For simplicity at this stage we invoke the equality of $u^i(q)$ and $v^i(q)$ as mentioned earlier and then the expression for $D_{qq'}(\omega)$ becomes,

$$
\begin{aligned}
D_{qq'}(\omega) = D^0_q(\omega)\Big[\delta_{-qq'} - 4\omega_q^{-1} D_4^{-1}(\omega)\{\lambda\, d_q(\omega) + D^0_{q'}(\omega)(\tau\, \tilde{d}_q(\omega) \\
- \lambda\, \tilde{\tilde{d}}_q(\omega)\, \omega_{q'})\}\sum_{i=1}^{n} U^i(-q_1, -q')\Big] + (2\pi g)^2\, D^0_q(\omega)\, D^0_{q'}(\omega)\, \omega_{q'}^{-1} \\
\times \{[\omega_{q'}\chi_{qq'}(\omega) - 4\lambda\tilde{\Phi}_{qq'}(\omega)] - 4D_4^{-1}(\omega)\,[\lambda\tilde{\tilde{d}}_{q'}(\omega)\tilde{P}_{qq'}(\omega) \\
+ \tau\, \tilde{d}_{q'}(\omega)\tilde{Q}_{qq'}(\omega)]\} \\
- \frac{(4\pi g)^2\, D^0_q(\omega)\, D^0_{q'}(\omega)}{\omega_q\, \omega_{q'}\, D_4(\omega)}\{[\lambda d_q(\omega)(\omega_{q'}\, \tilde{\Phi}_{qq'}(\omega) - 4\lambda\, \tilde{\tilde{\Phi}}_{qq'}(\omega)) \\
- \tau\tilde{d}_q(\omega)(\omega_{q'}\, \tilde{M}_{qq'}(\omega) - 4\lambda\, \tilde{\tilde{M}}_{qq'}(\omega)) + \lambda\tilde{\tilde{d}}_q(\omega)(\omega_{q'}\, \tilde{N}_{qq'}(\omega) \\
- 4\lambda\, \tilde{\tilde{N}}_{qq'}(\omega))] - 4D_4^{-1}(\omega)\,[\lambda d_q(\omega)(\lambda\tilde{\tilde{d}}_{q'}(\omega)\tilde{\tilde{P}}_{qq'}(\omega) + \tau\tilde{d}_{q'}(\omega)\tilde{\tilde{Q}}_{qq'}(\omega)) \\
- \tau\tilde{d}_q(\omega)(\lambda\tilde{\tilde{d}}_{q'}(\omega)\,\tilde{\tilde{P}}'_{qq'}(\omega) + \tau\tilde{d}_{q'}(\omega)\,\tilde{\tilde{Q}}'_{qq'}(\omega)) \\
+ \lambda\tilde{\tilde{d}}_q(\omega)(\lambda\tilde{\tilde{d}}_{q'}(\omega)\,\tilde{\tilde{P}}''_{qq'}(\omega) + \tau\tilde{d}_{q'}(\omega)\,\tilde{\tilde{Q}}''_{qq'}(\omega))]\}
\end{aligned}
\tag{22}
$$

where

$$\tilde{d}_q(\omega) = \pi\,[(\omega_q - a\lambda) + \pi\lambda\,(\omega_q\, D_{00}(\omega) - D_{01}(\omega)], \tag{22a}$$

$$\tilde{\tilde{d}}_q(\omega) = \pi\,[1 + \pi\,\tau\,(\omega_q\, D_{02}(\omega) - D_{03}(\omega))], \tag{22b}$$

$$d_q(\omega) = D_4(\omega) + \tau\,\tilde{d}_q(\omega)\, D_{02}(\omega) - \lambda\,\tilde{\tilde{d}}_q(\omega)\, D_{00}(\omega), \tag{22c}$$

$$\tilde{\Phi}_{qq'}(\omega) = \sum_{i=1}^{n} u^i(-q)\,\bar{\phi}^i_{q'}(\omega), \tag{23a}$$

$$\tilde{M}_{qq'}(\omega) = \sum_{i=1}^{n} u^i(-q)\,\bar{M}^i_{q'}(\omega), \tag{23b}$$

$$\tilde{N}_{qq'}(\omega) = \sum_{i=1}^{n} u^i(-q)\,\bar{N}^i_{q'}(\omega), \tag{23c}$$

$$\tilde{\tilde{\Phi}}_{qq'}(\omega) = \sum_{i,j=1}^{n} \sum_{q_1} u^i(-q)\, u^j(-q')\, u^j(q_1)\, \bar{\Phi}^j_{q_1}(\omega), \tag{24a}$$

$$\tilde{\tilde{M}}_{qq'}(\omega) = \sum_{i,j=1}^{n} \sum_{q_1} u^i(-q)\, u^j(-q')\, u^j(q_1)\, \bar{M}^j_{q_1}(\omega), \tag{24b}$$

$$\tilde{\tilde{N}}_{qq'}(\omega) = \sum_{i,j=1}^{n} \sum_{q_1} u^i(-q)\, u^j(-q')\, u^j(q_1)\, \bar{N}^j_{q_1}(\omega), \tag{24c}$$

$$\tilde{P}_{qq'}(\omega) = \tilde{N}_{qq'}(\omega) - \lambda\, D_{00}(\omega)\, \tilde{\phi}_{qq'}(\omega), \tag{25a}$$

$$\tilde{Q}_{qq'}(\omega) = \tilde{M}_{qq'}(\omega) - \lambda\, D_{02}(\omega)\, \tilde{\phi}_{qq'}(\omega), \tag{25b}$$

$$\tilde{\tilde{P}}_{qq'}(\omega) = \tilde{\tilde{N}}_{qq'}(\omega) - \lambda\, D_{00}(\omega)\, \tilde{\tilde{\phi}}_{qq'}(\omega)$$

$$= (2\pi g)^{-1} \sum_{i,j=1}^{n} \sum_{q_1} u^i(-q)\, u^j(-q')\, u^j(q_1)\, \bar{P}^j_{q_1}(\omega), \tag{26a}$$

$$\tilde{\tilde{P}}'_{qq'}(\omega) = (2\pi g)^{-1} \sum_{i,j=1}^{n} \sum_{q_1} u^i(-q)\, u^j(-q')\, u^j(q_1)\, D^0_{q_1}(\omega)\, \bar{P}^j_{q_1}(\omega), \tag{26b}$$

$$\tilde{\tilde{P}}''_{qq'}(\omega) = (2\pi g)^{-1} \sum_{i,j=1}^{n} \sum_{q_1} u^i(-q)\, u^j(-q')\, u^j(q_1)\, \omega_{q_1}\, D^0_{q_1}(\omega)\, \bar{P}^j_{q_1}(\omega), \tag{26c}$$

$$\tilde{\tilde{Q}}_{qq'}(\omega) = \tilde{\tilde{M}}_{qq'}(\omega) - \lambda\, D_{02}(\omega)\, \tilde{\tilde{\phi}}_{qq'}(\omega)$$

$$= (2\pi g)^{-1} \sum_{i,j=1}^{n} \sum_{q_1} u^i(-q)\, u^j(-q')\, u^j(q_1)\, \bar{Q}^j_{q_1}(\omega), \tag{27a}$$

$$\tilde{\tilde{Q}}'_{qq'}(\omega) = (2\pi g)^{-1} \sum_{i,j=1}^{n} \sum_{q_1} u^i(-q)\, u^j(-q')\, u^j(q_1)\, D^0_{q_1}(\omega)\, \bar{Q}^j_{q_1}(\omega), \tag{27b}$$

$$\tilde{\tilde{Q}}''_{qq'}(\omega) = (2\pi g)^{-1} \sum_{i,j=1}^{n} \sum_{q_1} u^i(-q)\, u^j(-q')\, u^j(q_1)\, \omega_{q_1}\, D^0_{q_1}(\omega)\, \bar{Q}^j_{q_1}(\omega). \tag{27c}$$

The quantities defined in equations (23) to (27) depend explicitly on the impurity coordinates; and hence these have to be averaged over all configurations of the *n*-

impurities. On performing the configurational averaging (Tripathi and Behera 1974) each of these quantities become proportional to the impurity concentration $c\ (\equiv n/N)$ and to $\delta_{-qq'}$, the latter indicating that the translational invariance of the system is regained through this averaging procedure. With this (22) reduces to

$$D_{-qq}(\omega) = D_q^0(\omega)\Big[1 + (2\pi g)^2 \chi_{-qq}(\omega)\ D_q^0(\omega) - cD_q^{-1}(\omega)\Big\{\mathscr{D}_{qq}(\omega) + (2\pi g)^2\Big[2\mathscr{D}_{qq}(\omega)\chi_{-qq}(\omega) - \omega_q^{-1}\ D_q^{-1}(\omega)\Big(\sum_{q_1}\mathscr{D}^2_{qq_1}(\omega)\ \omega_{q_1}\chi_{-q_1q_1}(\omega)\Big)\Big]\ D_q^0(\omega)\Big\}\Big] \tag{28}$$

where $$\mathscr{D}_{q_1q_2}(\omega) = \lambda\ d_{q_1}(\omega) - (\tau\ \tilde{d}_{q_1}(\omega) - (\lambda\ \omega_{q_2}\ \tilde{\tilde{d}}_{q_1}(\omega))\ D^0_{q_2}(\omega) \tag{29}$$

2.2 *Case II: Impurities characterized by λ and α*

In this case it is assumed that at the impurity site besides a change in the mass of the atom, the electron phonon coupling constant also changes locally. So the impurity Hamiltonian is given by (6) with the force constant change parameter τ equated to zero. The calculation of the phonon Green's function equation (10) for this case follows exactly a similar procedure as detailed in § 2·1, and for $q' = -q$ the result is .

$$D_{-qq}(\omega) = D_q^0(\omega)\Big[1 + (2\pi g)^2\chi_{-qq}(\omega)\ D_q^0(\omega) - cD^{-1}(\omega)\Big\{\lambda\ R_q(\omega) + (2\pi g)^2\lambda\ D_q^0(\omega)\Big(2R_q(\omega)\chi_{-qq}(\omega) - \lambda\,\omega^{-1}\ D^{-1}(\omega)\sum_{q_1}\omega_{q_1}R^2_{q_1}(\omega)\chi_{-q_1q_1}(\omega)\Big) - 8\pi^2 g\,\alpha\ D(\omega)\ D_q^0(\omega)\Big(1 - \lambda\,\omega_q^{-1/2}\ D^{-1}(\omega)\sum_{q_2}\sqrt{\omega}_{q_2}R_{q_2}(\omega)\Big) \times\Big(\chi_{-qq}(\omega) - \lambda\,\omega_q^{-1/2}\ D^{-1}(\omega)\sum_{q_1}\sqrt{\omega}_{q_1}R_{q_1}(\omega)\chi_{-q_1q_1}(\omega)\Big)\Big\}\Big], \tag{30}$$

where $$R_q(\omega) = 1 + \pi\omega_q\ D_q^0(\omega) \tag{31}$$

In calculating (30) terms proportional to α^2 have been neglected.

It is straightforward to check that in the absence of impurities ($c = 0$) both (28) and (30) reduce to

$$D_{-qq}(\omega) = D_q^0(\omega)\ [1 + (2\pi g)^2\chi_{-qq}(\omega)\ D_q^0(\omega)], \tag{32}$$

which gives the usual phonon self energy

$$\sum_q(\omega) = 4\pi g^2\,\omega_q\,\chi_{-qq}(\omega), \tag{33}$$

due to the electron-phonon interaction.

On setting $\tau = 0$ and $\alpha = 0$ respectively, (28) and (30) reduce to

$$D_{-qq}(\omega) = D_q^0(\omega)\Big[1 + (2\pi g)^2 \chi_{-qq}(\omega)\, D_q^0(\omega) - c\lambda\, D^{-1}(\omega)\Big\{\ldots R_q(\omega) + (2\pi g)^2\Big(2R_q(\omega)\chi_{-qq}(\omega) - \lambda\,\omega_q^{-1}\, D^{-1}(\omega)\sum_{q_1}\omega_{q_1} R_{q_1}^2(\omega)\,\chi_{-q_1 q_1}(\omega)\Big) D_q^0(\omega)\Big\}\Big], \tag{34}$$

which is the result for impurities characterized by only a mass change (Behera 1981).

2.3 *Evaluation of the response function* $\chi_{-qq}(\omega)$

It is evident from (28) and (30) that the phonon self-energy depends on the electron response function $\chi_{-qq}(\omega)$ (equation (14)). This quantity when evaluated for a perfect normal metal gives rise to the well-known Köhn anomaly in the phonon dispersion curve. However, since we are interested in the phonon Raman scattering in the superconducting state of 2H-$NbSe_2$, it is necessary to evaluate $\chi_{-qq}(\omega)$ with the BCS Hamiltonian (equation (3)) for $q = 0$ (Balseiro and Falicov 1980). This results in

$$\chi_{00}(\omega) = (\Delta/\pi)\sum_k \frac{\langle C_{k\uparrow}^\dagger\, C_{-k\downarrow}^\dagger\rangle}{E_k}\left[\frac{1}{\omega - 2E_k} - \frac{1}{\omega + 2E_k}\right], \tag{35}$$

where the anomalous correlation function $\langle C_{k\uparrow}^\dagger\, C_{-k\downarrow}^\dagger\rangle$ is given by

$$\langle C_{k\uparrow}^\dagger\, C_{-k\downarrow}^\dagger\rangle = (\Delta/2E_k)\tanh(\beta E_k/2), \tag{36}$$

and

$$E_k = (\epsilon_k^2 + \Delta^2)^{1/2} \text{ with } \beta = 1/k_B T. \tag{37}$$

On evaluating (35) together with (36) and (37) at $T = 0$, one gets

$$\chi_{00}(\omega) = -\frac{4\Delta^2\rho_0}{\pi\omega(4\Delta^2 - \omega^2)^{1/2}}\tan^{-1}\frac{\omega}{(4\Delta^2 - \omega^2)^{1/2}}\,; \text{ for } \omega < 2\Delta. \tag{38}$$

Where ρ_0 is the electron density of states at the Fermi level.

2.4 *Einstein model calculation*

It has been pointed out in § 2.3 that only phonons with wave vector $q = 0$ contribute to the Raman scattering process. In this limit the phonon that gets involved in the process is the transverse optic one. Hence we approximate the vibrational spectrum of the host crystal by the simple Einstein model with only one wave-vector-independent phonon of frequency ω_0. When (28) and (34) are evaluated in this model, the excitation spectra of the system for the two cases are respectively given by the solutions of the equations

$$(x^2 - 1)\,[1 + c\,F_1(\lambda, \tau, x)] + [1 + 2\,c\,F_2(\lambda, \tau, x) + c\,F_2^2(\lambda, \tau, x)] \times \sum_0^{BF}(y) = 0, \tag{39}$$

where $$F_1(\lambda, \tau, x) = [\lambda - \tau(1-\lambda)]\,[x^2 - (1-\lambda)(1+\tau)]^{-1} \tag{40a}$$

$$F_2(\lambda, \tau, x) = [\tau(1-\lambda) - \lambda x^2]\,[x^2 - (1-\lambda)(1+\tau)]^{-1} \tag{40b}$$

$$\sum_0^{BF}(y) \equiv 4\pi g^2 \omega_0 \chi_{00}(y)$$

$$= 4 s y^{-1}(1-y^2)^{-1/2} \tan^{-1}[y/(1-y^2)^{1/2}];\ y < 1. \tag{40c}$$

For $y > 1$, $\sum_0^{BF}(y)$ becomes complex, so that

$$\mathrm{Re}\sum_0^{BF}(y) = -4sy^{-1}(y^2-1)^{-1/2} \tanh^{-1}[y^{-1}(y^2-1)^{1/2}] \tag{40d}$$

$$\mathrm{Im}\sum_0^{BF}(y) = -2\pi s\, y^{-1}(y^2-1)^{-1/2}, \tag{40e}$$

with $$x = \omega/\omega_0,\ y = x\cdot(\omega_0/2\Delta) = \omega/2\Delta,\ s = \langle g^2 \rho_0\rangle/\omega_0, \tag{40f}$$

and $$(x^2-1)[1 + cF_1(\lambda, o, x)] + [1 - 2c\{g' - (1-g')x^2 F_1(\lambda, o, x)\} +$$

$$+ c(1+2g')x^4 F_1^2(\lambda, o, x)]\sum_0^{BF}(y) = 0 \tag{41}$$

where $$g' = \alpha/g, \tag{42}$$

$\sum_0^{BF}(y)$ being the Balseiro-Falicov expression for the phonon self-energy. It is needless to say that (39) and (41) reduce to (8) of Behera (1981) when τ and g' respectively are equated to zero.

3. Results and discussion

We shall discuss the significance of the results obtained in § 2 in the context of the Raman scattering measurement on the layered compound 2H-$NbSe_2$ by SK. As mentioned in § 1 in the absence of the impurities the BF model assumes the existence of a low lying CDW-AM phonon of frequency ω_0 which couples to the super-conducting gap excitations through electron-phonon interaction. In this case the phonon self-energy in the SC state is given by (40c); and has a square-root singularity at $y = 1$ (*i.e.* $\omega = 2\Delta$), giving rise to a peak in the phonon density of states around 2Δ, which is identified with the low temperature peak about 16 cm^{-1} in the Raman scattering spectrum of 2H-$NbSe_2$. As can be seen from (40f) the strength of this peak

depends crucially on s, which is directly proportional to the square of the electron-phonon coupling constant g and varies inversely as the phonon frequency ω_0. Thus for the observability of this peak with appreciable strength the presence of a low frequency phonon which couples strongly with the SC electrons is essential, In the case of 2H-$NbSe_2$ the availability of the CDW-AM phonon around 40 cm^{-1} fulfils this requirement. But in samples, where CDW formation is inhibited, the only Raman active phonons are the normal transverse optic modes at 234 and 248 cm^{-1} which being of very high frequency suppress the observability of the SC gap excitations as has been confirmed by Sooryakumar *et al* (1981).

In the presence of the impurities the spectral function $S_q(\omega) = -2 \operatorname{Im} D_q(\omega)$, which is the quantity one measures in Raman scattering, is calculated by attributing a finite width (Γ) to the phonons ($\omega^2 \to \omega^2 + 2i\,\Gamma\omega$); and is given by

$$S_0(y) \propto \frac{2\gamma x}{\{(x^2-1)\,[1+c\,F_1(\lambda, o, x)] + [1-2c\,x^2\,F_1(\lambda, o, x) + c\,x^4\,F_1^2(\lambda, o, x)]\,\Sigma_0^{BF}(y)\}^2 + (2\gamma x)^2} \quad \text{for } y < 1; \tag{43}$$

and

$$S_0(y) \propto \frac{2\gamma x - \operatorname{Im}\Sigma_0^{BF}(y)}{\{(x^2-1)\,[1+c\,F_1(\lambda, o, x)] + [1-2c\,x^2\,F_1(\lambda, o, x) + c\,x^4\,F_1^2(\lambda, o, x)]\,\operatorname{Re}\Sigma_0^{BF}(y)\}^2 + \{2\gamma x - \operatorname{Im}\Sigma_0^{BF}(y)\}^2} \quad \text{for } y > 1. \tag{44}$$

where $$\gamma = \Gamma/\omega_0. \tag{45}$$

In writing (43) and (44), τ and g' are taken to be zero in (39) and (41) respectively. In doing so, we have been motivated by the fact that inclusion of τ and g' does not bring in any drastic modification in the qualitative features of the spectral function as is evident from the structures of these equations. Furthermore in (44) we have neglected the concentration-dependent terms in the effective phonon width.

In carrying out the numerical calculation of (43) and (44), the parameters are chosen as follows: $s = 0.1$, $\omega_0 = 36$ cm^{-1}, $2\Delta = 23$ cm^{-1} and $\Gamma = 10$ cm^{-1}, which fit the experimental data (Sooryakumar and Klein 1981). The results are plotted in figures 1-6 for different values of the impurity mass change parameter λ. Figure 1 shows the results for the perfect crystal ($c = 0$) as well as for an imperfect one containing light mass impurities with $M_I = M/4 \Longrightarrow \lambda = -3$. As is evident from (43) and (44), in the absence of electron-phonon interaction (*i.e.*, $\Sigma_0^{BF}(\omega) = 0$) the impurity mode (local or resonant) should be given by

$$1 + cF_1(\lambda, o, x) = 0;$$

which gives rise to a peak in $S_0(\omega)$ around $\omega_0(1-\lambda)^{1/2}$. However, because of its coupling to the SC gap excitations (*i.e.* $\Sigma_0^{BF}(\omega) \neq 0$) it splits into two peaks which is clear for the local mode shown in figure 1. It is also obvious from the figure that the effect of the local modes on the SC gap excitation peak is insignificant.

Figures 2 to 6 depict the situation for heavy mass impurities, in which case there is a low lying resonant mode. The mass change parameters are chosen such that we

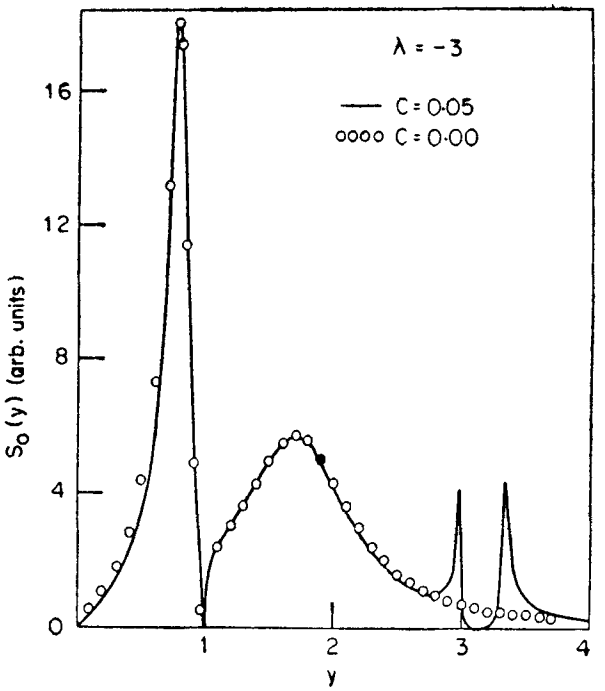

Figure 1. The spectral function $S_0(y)$ is plotted as a function of $y(\equiv \omega/2\Delta)$ when light mass impurities ($\lambda = -3$) are present and compared with that of the perfect crystal. The splitting of the local mode is clearly seen.

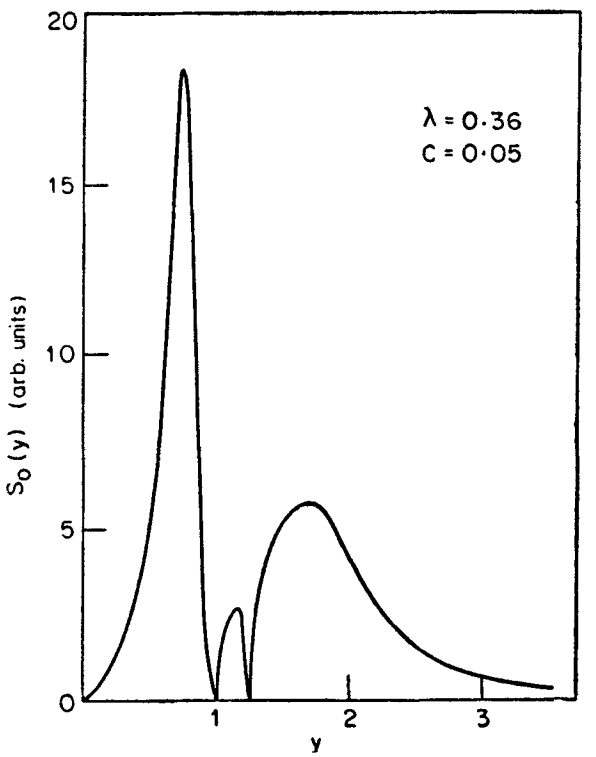

Figure 2. Plot of $S_0(y)$ versus y for heavy mass impurities ($\lambda = 0{\cdot}36$) which produce an impurity mode just below the CDW mode.

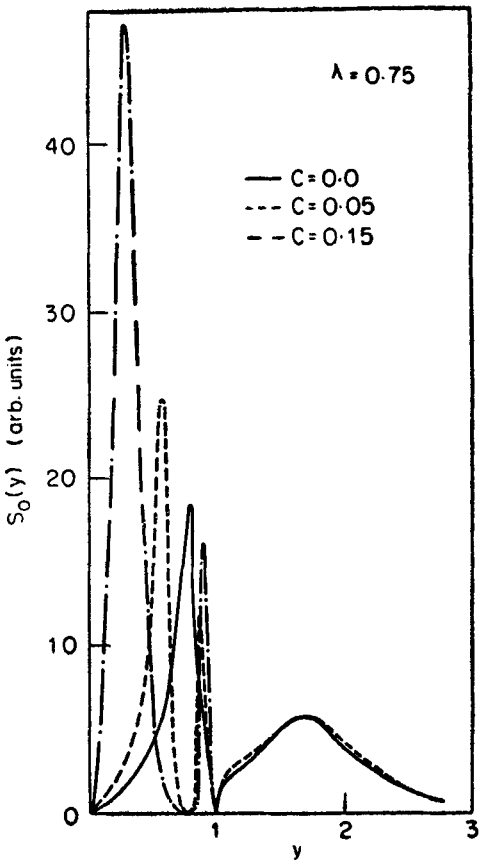

Figure 3. Plot of $S_0(y)$ versus y for $\lambda = 0{\cdot}75$ showing the concentration dependence of the modes due to the impurities, the CDW and the gap excitations. The enhancement of the gap excitation peak can be seen.

have three different situations (i) $2\Delta < \omega_I < \omega_0$ ($\lambda = 0{\cdot}36$ figure 2) (ii) $\omega_g < \omega_I < 2\Delta$ ($\lambda = 0{\cdot}75$ and $0{\cdot}7975$, figures 3 and 4 respectively) and (iii) $0 < \omega_I < \omega_g$ ($\lambda = 0{\cdot}8064$ and $0{\cdot}9$ figures 5 and 6 respectively), where ω_I and ω_g are respectively the frequencies of the impurity and the SC gap excitation modes. In the first case, the impurity mode produces a bifurcation in the broadened CDW-AM mode peak; without any significant change in the gap excitation peak. On the other hand, for case (ii), if ω_I lies close to 2Δ ($\lambda = 0{\cdot}75$) there appear three distinct peaks corresponding to ω_0, ω_I and ω_g. The strengths of both the peaks at ω_I and ω_g increase with concentration while the position of the latter gets shifted towards lower frequencies (figure 3). The other situation where ω_I is close to ω_g ($\lambda = 0{\cdot}7975$) is shown in figure 4. The important feature in this case is that again there is a splitting of the impurity mode, and an enhancement in the strength of the gap excitation peak. Finally for case (iii) there arise two different features which are depicted in figures 5 and 6. If the impurity mode lies just below ω_g ($\lambda = 0{\cdot}8064$), it splits into two (figure 5). On the other hand if ω_I is close to zero ($\lambda = 0{\cdot}9$) the splitting is absent (figure 6). However, in either case, the strengths of the impurity peaks get enhanced while that of the gap excitation peak decreases.

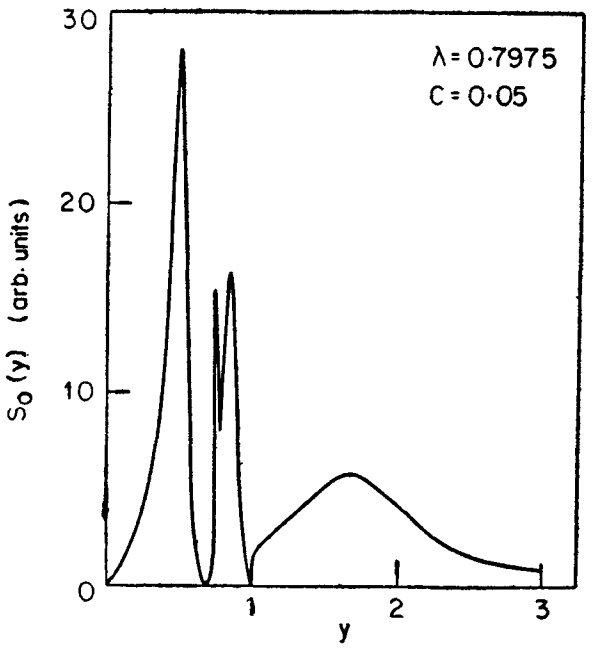

Figure 4. Plot of $S_0(y)$ versus y, for $\lambda = 0{\cdot}7975$, which shows the splitting of the resonant mode; when it lies just above the gap excitation peak.

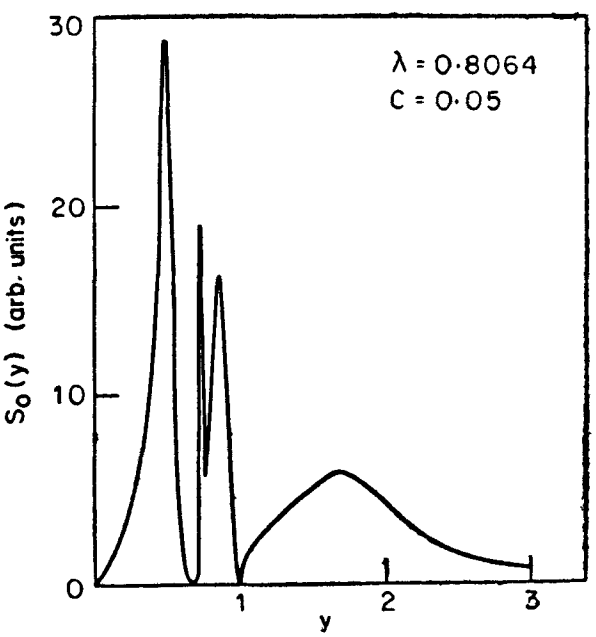

Figure 5. Same as in figure 4, for $\lambda = 0{\cdot}8064$, when the impurity mode falls just below the gap excitation peak.

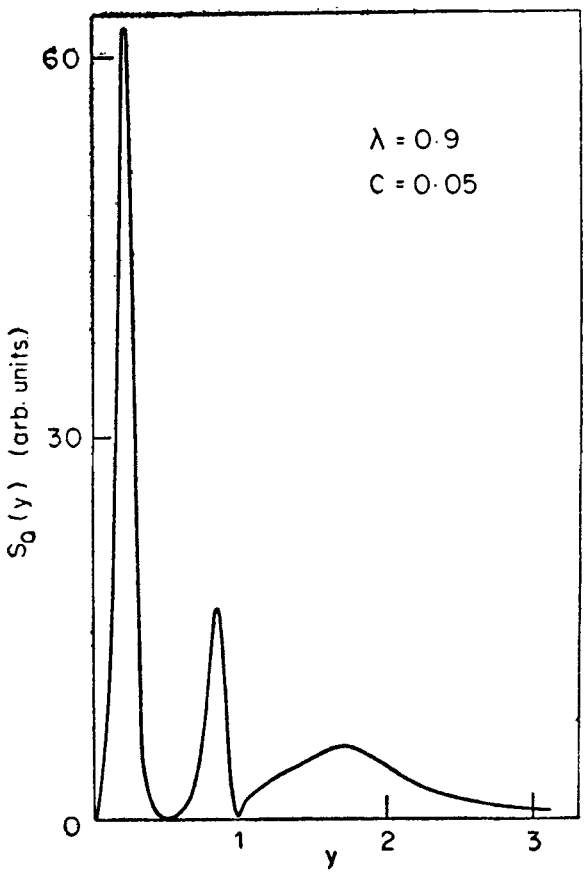

Figure 6. Plot of $S_0(y)$ versus y for $\lambda = 0{\cdot}9$, showing the enhancement of the impurity mode when its frequency is close to zero.

It should be pointed out that the distinct feature of this calculation is the prediction that there is a splitting of the impurity mode. However, the nature of the splitting depends peculiarly on the position of ω_I, as categorized above. In the case of the local mode the splitting occurs for all values of λ even though ω_I is far away from ω_g. In contrast the resonant mode splits only for such values of λ, when ω_I is below 2Δ and very near ω_g.

Sooryakumar *et al* (1981) have measured the Raman spectra of impure samples of 2H-$NbSe_2$ in the superconducting phase. For samples where the CDW formation is suppressed by the impurities, they fail to observe the SC gap excitation mode, which is a clear indication of the fact that the low lying CDW-AM mode couples strongly to the SC electrons. However, measurement in other samples, shows the existence of the CDW-AM mode, the SC gap excitation peak and a broad feature identified as the impurity mode (figures 11 and 12 of Sooryakumar *et al* 1981). In fact the impurity mode which lies above the CDW-AM phonon shows some structure when cooled to 2°K. Even though the experimental data of Sooryakumar *et al* were not analyzed to study the behaviour of the impurity mode, we conjecture that the observed structure in a way substantiates our prediction regarding the splitting of the local mode. Furthermore it should be noted that the imperfections in these samples are

thought to be due to iodine and structural defects, which depend on the growth procedure and not substitutional defects as required by our calculation. Therefore we suggest that in order to confirm the theoretical predictions the experiments be repeated with samples having substitutional defects.

Most of the interesting features can be observed only when the impurity mode falls below the CDW-AM phonon for which heavier mass impurities are needed. In case of 2H-$NbSe_2$, this may apparently look difficult, as the host atom (Nb) is already too heavy. However this difficulty can be circumvented by substituting even lighter mass impurities which produce large force constant softening (Behera 1979).

4. Conclusion

In concluding we summarize the main results of the present paper. The BF theory is extended to take into account the effect of substitutional non-magnetic impurities on the observed SC gap excitation peak in the Raman spectrum of 2H-$NbSe_2$. It was assumed that the impurities perturb the host crystal because of (i) the difference in mass, (ii) the change in the nearest neighbour force constants and (iii) local modification of the electron-phonon interaction. The phonon self-energy due to these perturbations, is calculated to lowest order in the impurity concentration. The results are analysed in the $q = 0$ limit assuming the Einstein oscillator model for the host phonons. A special feature of the calculation is the splitting of the impurity mode (local/resonant) into two in the SC state. An enhancement in the strength of the SC gap excitation peak is predicted whenever its position is close to that of the impurity mode. The existing experimental data on imperfect samples of 2H-$NbSe_2$ was discussed in the light of the present calculation. For complete verification of our predictions it was suggested that experiments be performed with samples containing substitutional impurities which can produce low lying resonant modes.

It is expected that even in non-CDW super-conductors, such gap excitations should in principle be observed if a suitable low lying phonon with frequency comparable to 2Δ can be produced. Presence of heavy mass impurities easily gives rise to such modes. However, in the present calculation this expectation does not materialize, because the strength of the effective coupling between the phonon and the SC electrons turns out to be too weak.

We have made a number of simplifying assumptions in this paper. They are: (i) Although there are several Raman active phonons in the system, only the CDW-AM mode is considered and is assumed to have the Einstein frequency ω_0 from which the impurity mode originates, (ii) All the calculations are carried out for $q = 0$, whereas the more appropriate limit corresponds to small values of q. (iii) The appropriate vertex corrections including the effect of the Coulomb interaction between electrons, which is necessary for the gauge invariance of the theory, was not accounted for. Calculations are in progress to improve upon the deficiencies mentioned in (ii) and (iii).

Yet another assumption is that the effect of non-magnetic impurities on the formation of the CDW and hence on the frequency ω_0 of the CDW-AM phonon is neglected. This will be the subject matter of a future investigation.

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