MICROSCOPIC THEORY OF CHARGES DENSITY WAVE INSTABILITY IN $NbSe_2$

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MICROSCOPIC THEORY OF CHARGE DENSITY WAVE INSTABILITY IN $NbSe_2$ +

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The microscopic theory of Sinha and Harmon for electronically driven lattive instabilities[1] is used to explain the "Kohn-like" anomalies in the Σ_1 phonon branch and the observed incommensurate superlattice Bragg peak in 2H-$NbSe_2$, characteristic of the charge density wave at low temperatures in the neutron scattering experiments of Moncton et al.[2] In accordance with the APW and LCAO band-structure calculations of Mattheiss of 2H-$NbSe_2$, we have assumed the presence if three narrow d bands of atomic symmetry xy, x^2-y^2 and $3z^2-r^2$ at the Fermi level. Thus the conduction-band wave function is represented by a linear combination of tight-binding Gaussian atomic orbitals with neglect of the variation of the radial wave function across the bands. The screened electron-ion interaction and the Coulomb energy of the charge fluctuation on the d shells of Nb atom is represented by a pseudopotential screened by the Lindhard dielectric function. The phonon eigen vectors needed for estimating the electron-phonon interaction were calculated using a simple force constant model. In agreement with the experimental results, we have found that the phonon frequencies for the Σ_1 and Σ_3 branches are very strongly renormalized as one approaches the zone boundary. By introducing the electronic relaxation effects a central peak appears at the q vector of the instability and the actual phonon renormalization is partially suppressed. This explains the superlattice Bragg peaks observed at low temperatures and "Kohn-like" anomalies in the Σ_1 phonon branch of $NbSe_2$.

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1 S.K. Sinha and B.N. Harmon, Superconductivity in d- and f-band metals, ed. by D.H. Douglas (1976).

2 D.E. Moncton, J.D. Axe and F.J. Disalvo, Phys. Rev. Lett. 34, 734 (1975)

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The occurrence of periodic lattice distances (PLD) in the layered transition metal chalcogenides has been studied extensively in the last few years[1-4]. Such lattice distortions, also referred to as "Charge Density Waves" are believed to arise as a result of the very anisotropic nature of the Fermi surface in these quasi-two-dimensional materials, and in particular to the nesting features of the Fermi surface. Such features give rise to an enhancement at certain $\vec{q}$-values of the (non-interacting) polarizability $\chi_o(\vec{q})$ defined by

$$\chi_o(\vec{q}) = 2\sum_k (n_k - n_{k+q})/(E_k - E_{k+q}) \quad (1)$$

where k denotes the electronic state of energy E_k and occupation number n_k (Eq. (1) should strictly speaking include matrix elements. However (1) is the form for which numerical calculations have actually been performed, and further, only bands at the Fermi level have been included in the calculations[5,6]). Assuming only diagonal screening by the electron system of the electron-phonon interaction, the theory of Chan and Heine[7] has usually been involved to show that the phonon softening is given by

$$\omega_q^2 = \omega_q^{o2} - g_q^2 \chi_o(\vec{q})/(1 + v_{eff}(\vec{q})\chi_o(\vec{q})) \quad (2)$$

where ω_q^o is the unrenormalized frequency, g_q is the electron-phonon coupling coefficient (whose $\vec{q}$-dependence is generally ignored), and $v_{eff}(\vec{q})$ is the effective electron-electron interaction which is the sum of Coulomb and exchange and correlation parts.

Calculations by Myron and Freeman[5] for 1T-TaS_2 and 1T-$TaSe_2$ and by Ricco[6] for 2H-$NbSe_2$ using Eq.(1) for the bands only at the Fermi level have shown that there is indeed a peak at approximately the wavevector ($\vec{q}=0.33\vec{a}^*$) corresponding to the PLD, which would thus yield, according to Eq.(2), the maximum softening of the phonons at this wavevector.

However, there are several unsatisfactory aspects to the above theory. In the first place, the "peak in $\chi_o(\vec{q})$", particularly in 2H-$NbSe_2$, is relatively small on a large background and it is

difficult to understand how the whole phenomenon arises simply because of this somwhat subtle feature; secondly, there are other nesting features of the Fermi surface which give rise to equally large peaks along other directions, e.g. along the $\vec{b}^*$ axis, and it is difficult to understand why the lattice prefers to have its instability along the $\vec{a}^*$ axis for all these compounds on the basis of $\chi_0(\vec{q})$ alone. Finally, the phonon branches actually do not show pronounced softening as the ordering temperature is approached[2]. Instead, a "central peak" is observed in the neutron scattering which rapidly increases to critical-like scattering as the ordering temperature is approached.

A more detailed theory must take into account the $\vec{q}$-dependence of the electron-phonon interaction and the more complicated screening when the wavefunctions involved are d-orbitals rather then a free-electron gas, and hence necessarily must allow for the off-diagonal nature of the screening. Such theories have been developed recently[8,9] and are reviewed in a paper at this Conference[10]. We shall refer to the latter paper henceforth as I.

Using the results of I, generalized to the case of crystals with more than one atom/cell, the expression for the normal mode frequencies is given by

$$\omega_{qj}^2 = \omega_{qj}^{o2} - \sum_{\alpha\beta} \sum_{\kappa_1\kappa_2\kappa_3\kappa_4} \sum_{\mu_1\mu_2} (M_{\kappa_1} M_{\kappa_4})^{-1/2} e_\alpha^*(\kappa_1|qj) \times Q_{\mu_1}^{\alpha,\kappa_1\kappa_2}(-\vec{q})\, \chi_{\mu_1\mu_2}^{\kappa_1\kappa_2}\, Q_{\mu_2}^{\beta,\kappa_4\kappa_3}(\vec{q})\, e_\beta(\kappa_4|qj) \qquad (3)$$

where the index κ stands for a particular basis atom in the unit cell (of mass M_κ) with associated eigenvector $e_\alpha(\kappa|qj)$; μ_1 stands for a pair of indices (ξ_1, ξ_2) denoting atomic-like orbitals between which a virtual transition is induced for a particular charge fluctuation (CF) excited by the phonon. (We neglect, for simplicity, overlap between orbitals in the present calculation). $\chi_{\mu_1\mu_2}^{\kappa_1\kappa_2}(\vec{q})$ is the (static) density response func-

tion connecting CF's of type μ_1 on site κ_1, with those of type μ_2 on site κ_2.

$\left[\sum_{\kappa,\alpha} Q_{\mu_1}^{\alpha,\kappa\kappa'}(\vec{q})\, e_\alpha(\kappa|qj)\, M_\kappa^{-1/2}\right]$

is the coupling coefficient between the displacements of the ions for mode (qj) and CF's of type μ_1 on site κ'

For our present purposes, we are interested only in a semi-quantitative understanding of the microscopic origin of the lattice instability and hence we focus our attention on CF's involving only the d-bands at the Fermi level. As discussed in I, the other types of CF's may be regarded as screening the d-shell fluctuations and the d-electron-ion interactions, as well as renormalizing ω_{qj}^0.. $Q^{\alpha,\kappa\kappa_1}_{\mu_1}$ may be then be written in the form given in Eq.(17) of I (suitably generalized with appropriate phase factor to the case of a lattice with basis). The matrix $\underset{\sim}{\chi}$ is given by Eqs.(10) and(18) and (19) of I, suitably generalized to the case of a lattice with basis. For the calculations on 2H-$NbSe_2$, we used the results of Mattheiss[11] who showed that the d-bands around E_F are associated primarily with (x^2-y^2), (xy) and $(3z^2-r^2)$ d-orbitals on the Nb sites. This gives us 9 possible types of CF to consider on each Nb site, and since there are two such sites per unit cell, the size of the matrix $(\underset{\sim}{V}+\underset{\sim}{N}^{-1})$ was 18x18. The orbitals were taken as HFS atomic d-orbitals. Note that the $\underset{\sim}{N}$ matrix involves the function $\chi_0(\vec{q})$ (see Eq. (19) of I). For the screening function $\epsilon_s(\vec{q})$, a Lindhard function with k_f=0.17 was assumed. The ionic radii for the Nb and Se ions were taken as 2.64, 2.16 respectively (a.u.), and the effective ionic charges as 0.5, -0.25 respectively. The Hubbard U for same-site Nb CF interactions (see Eq.(18) of I) was taken as 2eV. The phonon eigenvectors $e_\alpha(\kappa|qj)$ were evaluated for $\vec{q}$ along ΓM by fitting an empirical force-constant model to the experimental neutron-scattering results for the frequencies of the Σ_1, Σ_3 and Σ_4 branches along ΓM.

Fig. 1 shows the $\vec{q}$-dependence of the quantity $\left[\sum_{\kappa\beta} Q_{\mu_2}^{\beta,\kappa\kappa'}(\vec{q})\, e_\beta(\kappa|qj)\, M_\kappa^{-1/2}\right]$

for the Σ_1 mode for μ_2 corresponding to an $(xy \rightarrow xy)$ CF, and κ' corresponding to Nb site 1. This represents the coupling between monopole-type CF's on this site to the ionic displacements in this mode. It may be seen that this quantity peaks at around $q=0.35\vec{a}^*$, showing that the lattice has a natural "geometrical" enhancement at such q-values for coupling CF's of this type to this phonon mode. Fig. 2 shows the $\vec{q}$-dependence of the corresponding element of $\underset{\sim}{\chi}$, i.e. $(\underset{\sim}{V}+\underset{\sim}{N}^{-1})^{-1}$, assuming (a) $\chi_0(\vec{q})$ has no $\vec{q}$-dependence and is fixed at $n_d(E_F)$ and (b) using the actual $\chi_0(\vec{q})$ calculated by Ricco[6] from the energy bands. Fig. 3 shows the phonon softening $\Delta\omega^2$ vs. $\vec{q}$ along ΓM for the Σ_1 branch for the same two assumptions. One notices that even with a constant $\chi_0(\vec{q})$ the density response function is quite enhanced for sufficiently large $n_d(E_F)$ and helps the electron-phonon coupling to produce the phonon softening at the right $\vec{q}$-value. This is because of the smallness of certain elements of $(\underset{\sim}{V}+\underset{\sim}{N}^{-1})$ leading to enhancement of the CF response of the d-electrons. Using the actual $\chi_0(\vec{q})$ which has peaks built in due to Fermi surface nesting greatly enhances this resonant-like response and in fact the peak in $\chi_0(\vec{q})$ can " fine-tune" the actual position of the anomaly. The point is however, that the "background" on which this peak rides plays an important role in enhancing the response, as does the $\vec{q}$-dependence of the electron-ion coupling. Thus it appears that explanations based on Eq.(2) are rather too simplistic. (Note that in the Chan-Heine theory, $V_{eff}(\vec{q})$ is always positive, unlike the elements of the $\underset{\sim}{V}$ matrix in the formulation which includes local-field effects, (see the discussion in I), and hence resonant enhancement of the CF response is not possible).

In order to explain the occurrence of a central peak in the neutron scattering, we introduce a relaxation time for the electrons, as discussed in I, which introduces a complex phonon self-energy $\Delta\omega^2$ and results in a 3-peak structure in the neutron cross-section. Fig.4 shows the intensity of the central peak

as calculated using Eq. (25) of I for the calculation using Ricco's $\chi_0(\vec{q})$.

We thus see that the present model, although somewhat crude in its treatment of the electron-response and the electron-phonon interaction, has the essential qualitative features which are consistent with the experimental observations. The main purpose has been to show that near-instabilities with regard to d-shell CF's due to high $n_d(E_F)$ and the coupling of these CF's to the lattice displacements are as essential features of the physics of the lattice instabilities in these materials as are the Fermi surface effects.

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FIGURE CAPTIONS

Fig. 1. $\vec{q}$ dependence of real and imaginary parts of quantity $W(\vec{q})$ = along ΓM for the Σ_1 mode for an (xy→xy) orbital charge fluctuation.

Fig. 2. $\vec{q}$-dependence of (xy→xy),(xy→xy) component of $(V+\vec{M})^{-1}$ matrix along ΓM for a) constant $\chi_0(\vec{q})$(full line) and b)Ricco's $\chi_0(\vec{q})$(dashed line).

Fig. 3. Phonon softening for Σ_1 mode along ΓM (in absence of relaxation effects) for a) constant $\chi_0(\vec{q})$ (full line and b) Ricco's $\chi_0(\vec{q})$ (dashed line)

Fig. 4. Central peak intensity for Σ_1 mode along ΓM (with relaxation effects) for a) constant $\chi_0(\vec{q})$ (dashed l and b) Ricco's $\chi_0(\vec{q})$ (full line).

ELECTRON PHONON CONTRIBUTION TO PHONON SOFTENING

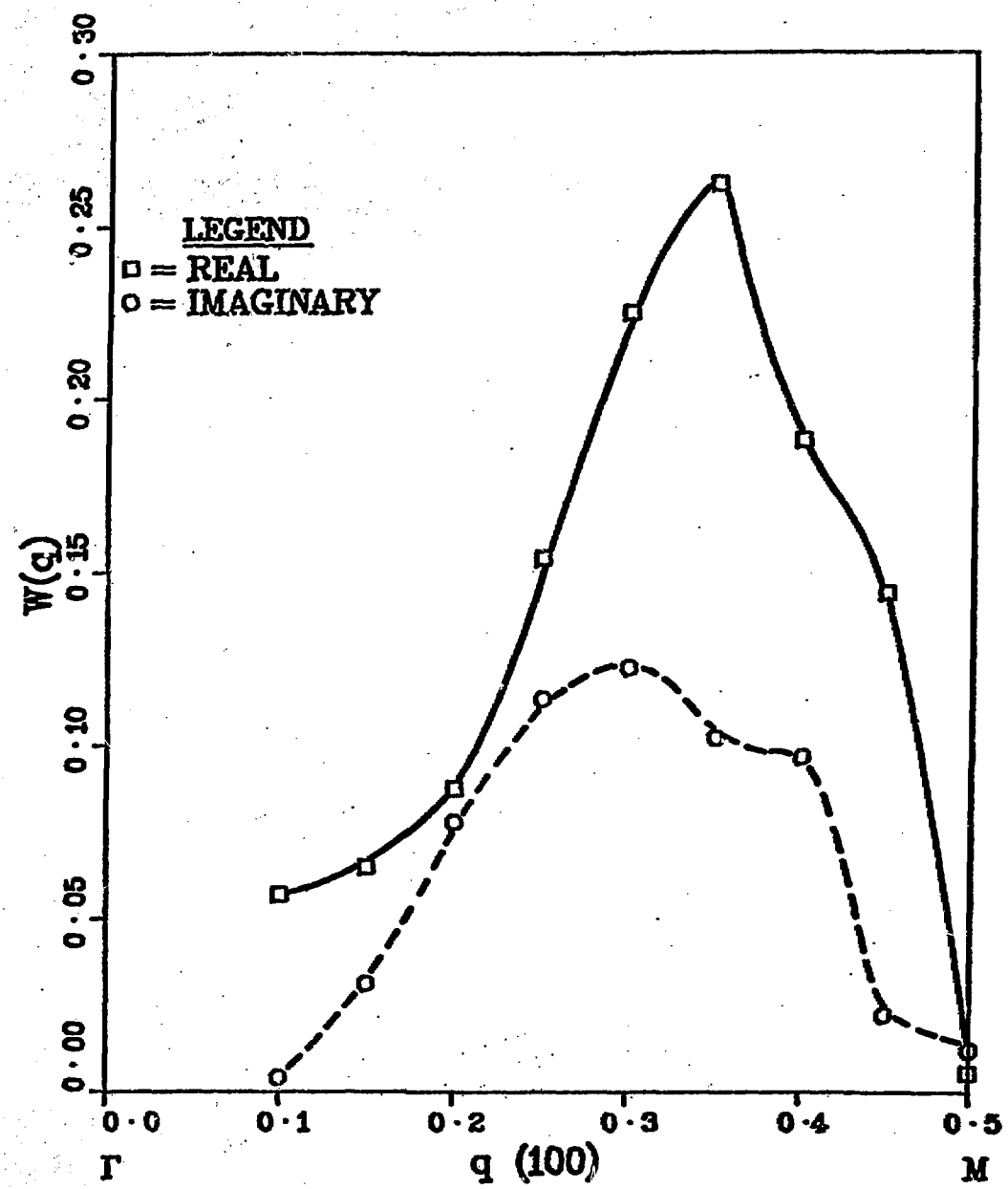

Fig. 1

COULOMB INTERACTION CONTRIBUTION TO PHONON SOFTENING

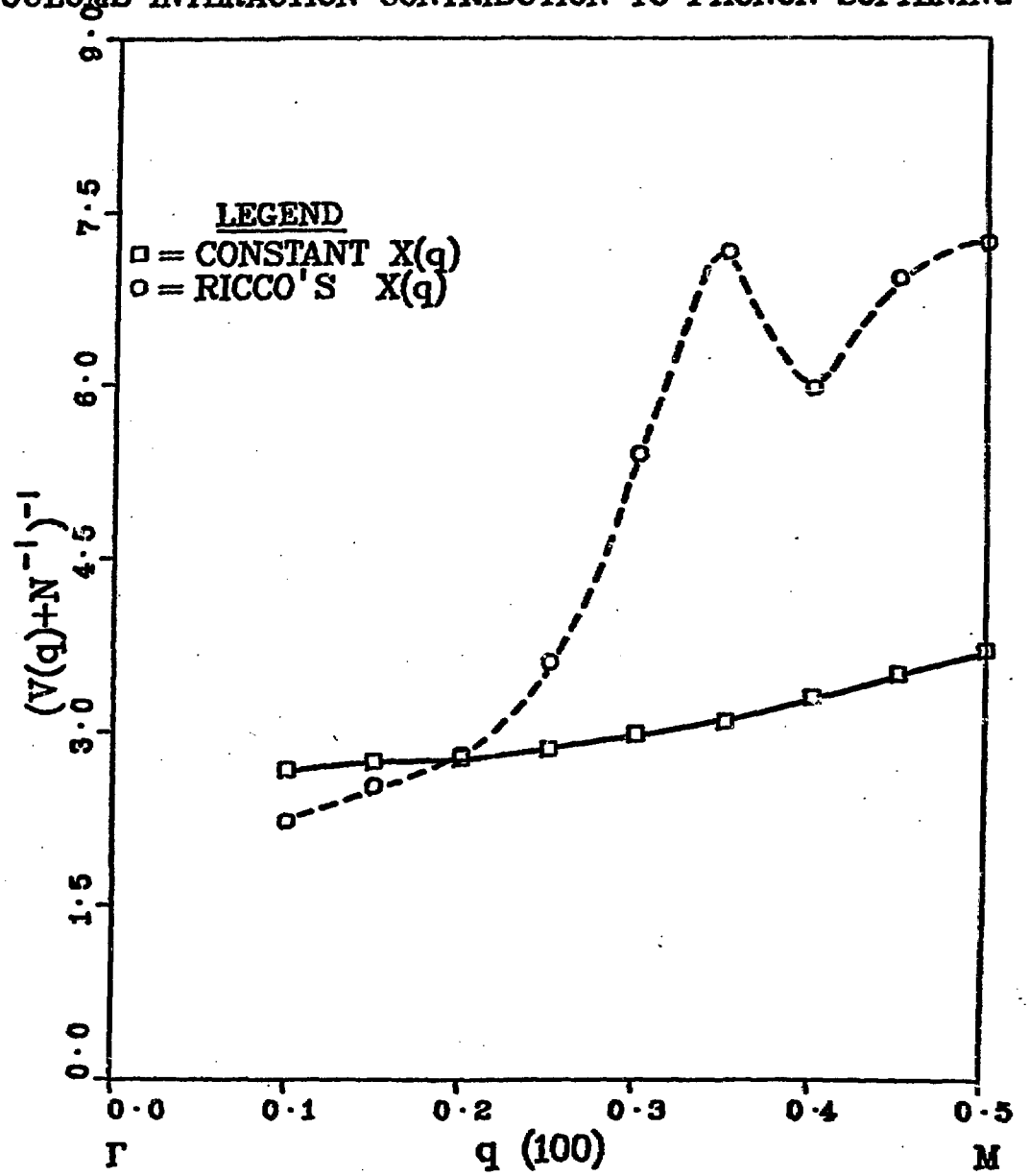

Fig. 2

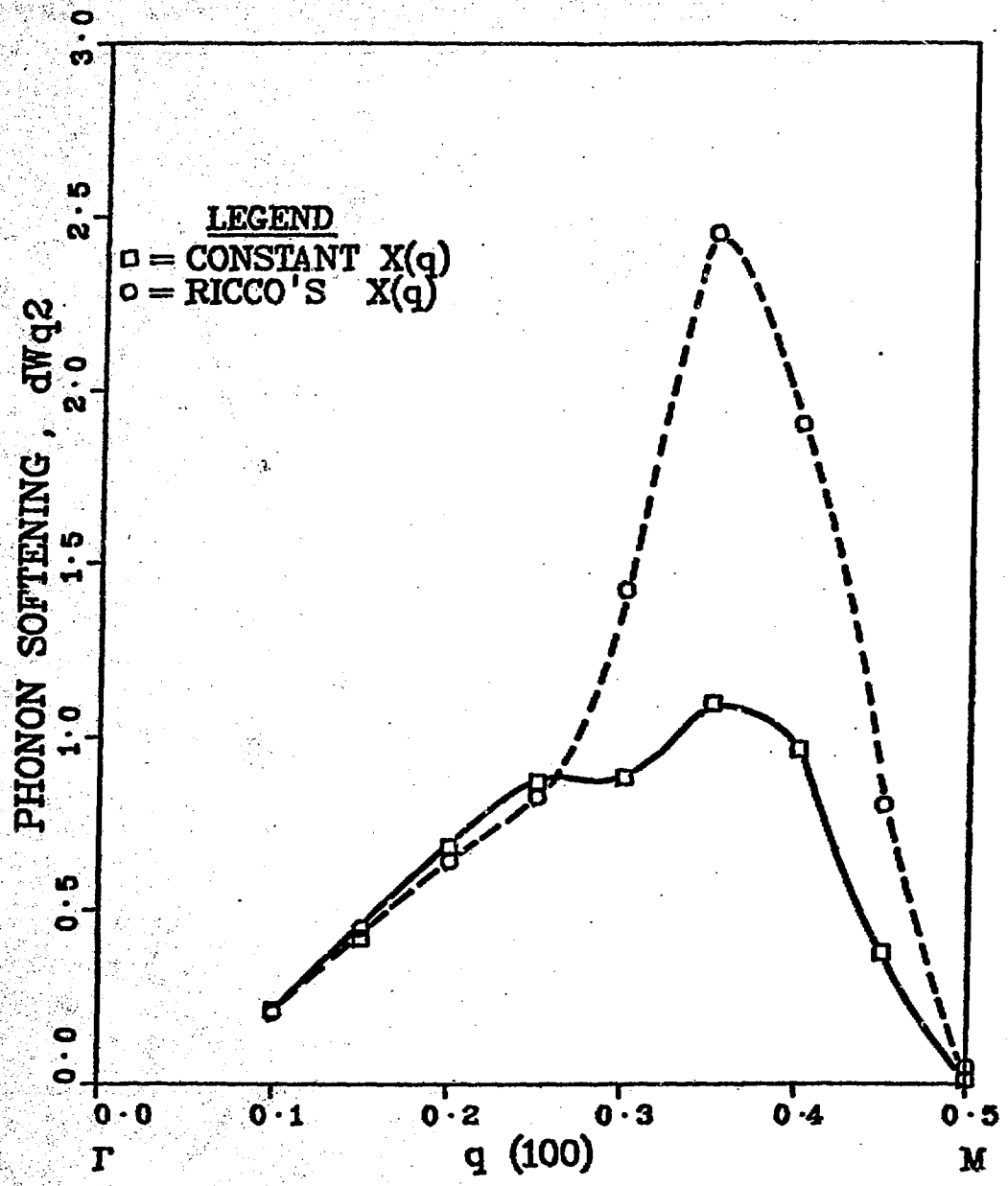
LEGEND
□ = CONSTANT X(q)
○ = RICCO'S X(q)
PHONON SOFTENING , dWq2
0·0
0·5
1·0
1·5
2·0
2·5
3·0
0·0
0·1
0·2
0·3
0·4
0·5
Γ
q (100)
M

Fig. 3

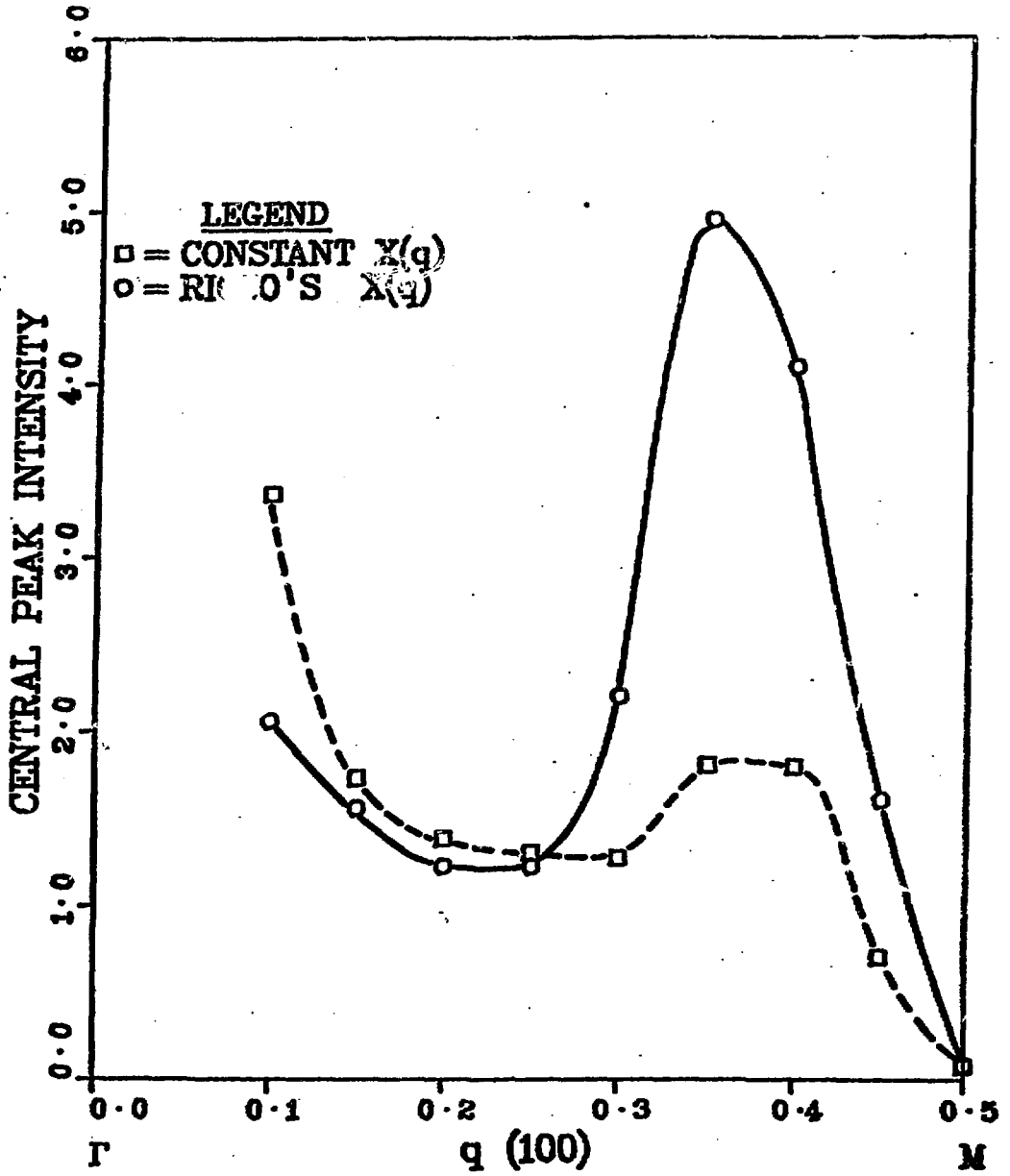
LEGEND
□ = CONSTANT X(q)
○ = RI(.0'S X(q)
CENTRAL PEAK INTENSITY
0·0
1·0
2·0
3·0
4·0
5·0
6·0
0·0
0·1
0·2
0·3
0·4
0·5
Γ
q (100)
M

Fig. 4