

Inelastic X-Ray Scattering as a Probe of Electronic Excitations; Solid and Liquid Metals

J. P. Hill

MASTER

Dept. of Physics, Brookhaven National Laboratory, Upton, USA.

Abstract

The use of inelastic x-ray scattering for the study of excitations in condensed matter systems is discussed with emphasis on the complementarity with inelastic neutron scattering. In particular, studies of electronic excitations in simple metals are detailed. A long standing controversy on the role of crystalline long range order on electron dynamics at intermediate momentum transfers is resolved by comparison of response functions obtained in the liquid and solid phase of Li, Na and Al. These data show that the overall shape of the response function is unchanged on melting, implying that it is not determined by the long range order of the ion-cores. Conversely, orientationally-independent fine structure disappears on melting and therefore must be attributed to band structure-induced transitions, not many-body effects as had previously been argued. At small q , the plasmon lifetime and dispersion remain unchanged on melting. Other experiments are also briefly reviewed.

1 Introduction

Traditionally, scattering investigations of excitations in condensed matter systems have been the purview of inelastic neutron scattering. In contrast, x-ray scattering has been primarily performed in the quasi-elastic (energy integrating) limit, for which the same-time correlation function is measured. Nevertheless, there are important strengths that x rays have to offer in the study of dynamic phenomena, and these are now beginning to be realized with the development of dedicated energy resolved x-ray scattering beamlines at a number of synchrotrons around the world.

In this paper, the advantages and disadvantages of inelastic x-ray scattering (IXS) are outlined, with particular emphasis on the study of electronic excitations. Results from an investigation of electron dynamics in liquid and solid metals are presented by way of an example. A comparison of the response in the liquid and solid phase reveals the role of the long range crystalline order in determining the dynamics of the conduction electrons. We conclude with a very brief survey of a number of other studies that have been performed on a variety of different systems, to provide a flavor of this rapidly growing field of study.

2 X-ray Cross-section

The double differential, non-resonant, x-ray cross-section is given by¹

$$\frac{d^2\sigma}{d\Omega d\omega} = r_o^2(\epsilon_i \cdot \epsilon_f) \left(\frac{\omega_f}{\omega_i}\right) S(\vec{q}, \omega), \quad (1)$$

with

$$S(\vec{q}, \omega) = \frac{1}{2\pi} \int dt e^{-i\omega t} \langle \rho_{\vec{q}}(t) \rho_{-\vec{q}}(0) \rangle, \quad (2)$$

where the dynamic structure factor, $S(\vec{q}, \omega)$ is the Fourier transform of the charge fluctuation spectrum and q and ω are, respectively, the momentum and energy transfers of the scattering process. Note that this is the same

¹The magnetic contributions to the x-ray cross-section have been ignored. While, in principle, these would give rise to inelastic magnetic scattering, such terms are expected to be extremely weak and will not be considered further here.

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correlation function as that measured by inelastic neutron scattering, except in the latter case it is the nuclear and magnetic densities that are probed.

Depending on the transferred momentum and energy, x-rays are sensitive to a variety of correlations: If q is much larger than the inverse of the inter-particle spacing, λ_c^{-1} , then interference effects between scattered amplitudes are negligible and single particle properties are measured. This is the Compton regime. Conversely, interference effects become important at smaller momentum transfers and collective excitations may be investigated. For energy transfers in the meV regime, excitations such as phonons are observed. X rays do not suffer the same kinematic constraints as neutrons and this provides some advantages in studying, for example, disordered systems. Specifically, one can measure dispersion relations out to relatively large energy transfers (20-30 meV) even for high values of the speed of sound, which is not possible with neutrons. Some very beautiful work has been done in this regime on liquids and glasses at the ESRF, beamline ID16, which has achieved an energy resolution of ~ 2 meV, with a flux of 10^9 photons s^{-1} (see for example refs [1, 2]).

In addition to the small energy transfer regime, x rays are also able to access very large energy transfers because of the high incident energy of the photon. For energy transfers on the order of eV, electronic excitations may be observed. electron energy loss spectroscopy (EELS) can also attain such energy transfers, however, IXS offers significant advantages over this technique. Specifically, the weakly interacting nature of x rays means that multiple scattering effects are negligible and hence the cross-section is always directly interpretable. In contrast, EELS data are dominated by multiple scattering effects beyond $q > \approx 1 \text{ \AA}^{-1}$. As we shall see, this is precisely where some of the most interesting physics of the electron gas lies. Further, x-rays are not too surface sensitive, relative to EELS, and sample environments are significantly simplified.

The region of (q, ω) -space that is accessible with inelastic x-ray scattering techniques is shown in fig 1, together with a number of other inelastic probes.

The disadvantage of IXS is the very low count rates; only a small fraction of the photons are scattered inelastically (for simple metals this fraction is $\sim 10^{-6}$) and the signal is typically limited by absorption. In practice, this means that for current generation synchrotrons the study of electronic excitations using non-resonant inelastic scattering is limited to materials with

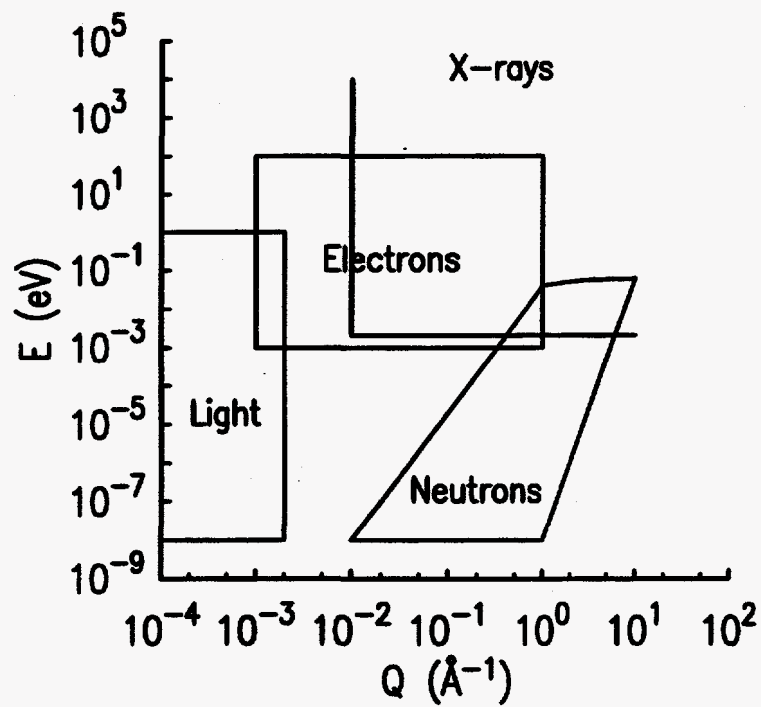


Figure 1: The accessible energy and momentum transfers of a variety of established inelastic scattering techniques, in comparison to inelastic x-ray scattering.

$Z < 30$.

The power of x-rays in the study of electronic excitations is partly derived from the direct relationship between the cross-section and the complex dielectric function, [3]

$$S(\vec{q}, \omega) = \frac{\hbar q^2}{2\pi e^2} \text{Im} \left(\frac{1}{\epsilon(\vec{q}, \omega)} \right). \quad (3)$$

This function may be calculated using various many-body approaches, most simply using the Random Phase Approximation (RPA), and x rays offer the unique ability to test such theories over all relevant q . Calculating $\epsilon(q, \omega)$ for the homogeneous electron gas (jellium model) in fact represents perhaps the oldest and most studied many-body problem in condensed matter physics and thus there is a great deal of interest in obtaining empirical input for such calculations.

Within the RPA, there are two regimes for the response of the electron liquid: At small q , the collective excitations, the plasmons, are expected to be well defined, long lived excitations, with an approximately quadratic dispersion. At larger q , the single particle excitations dominate, existing in a continuum band, and the response is expected to be broad and featureless. These general features are indeed seen in the x-ray data, as shown in fig. 2. However, as discussed below, discrepancies are observed on closer inspection. These data were taken on Li ($r_s=3.25$) at room temperature.

3 Experimental Details

The experiments discussed here were carried out at the wiggler beamline, X21 at the National Synchrotron Light Source, USA. A horizontally focusing miscut Si(220) monochromator delivered 2×10^{11} photons s^{-1} onto the sample in a line focus $10\text{mm} \times 0.5 \text{ mm}$ at 8 keV. The scattered radiation was collected by a spherically bent Si crystal, utilizing the Si(444) reflection to take advantage of the improved energy resolution of the back scattering geometry ($\theta = 86^\circ$).

In exact analogy with a neutron triple axis spectrometer, the incident energy, or final energy may be scanned independently. The momentum transfer is determined by the scattering angle. Typically, energy loss scans are performed by scanning the incident energy, keeping the final energy constant,

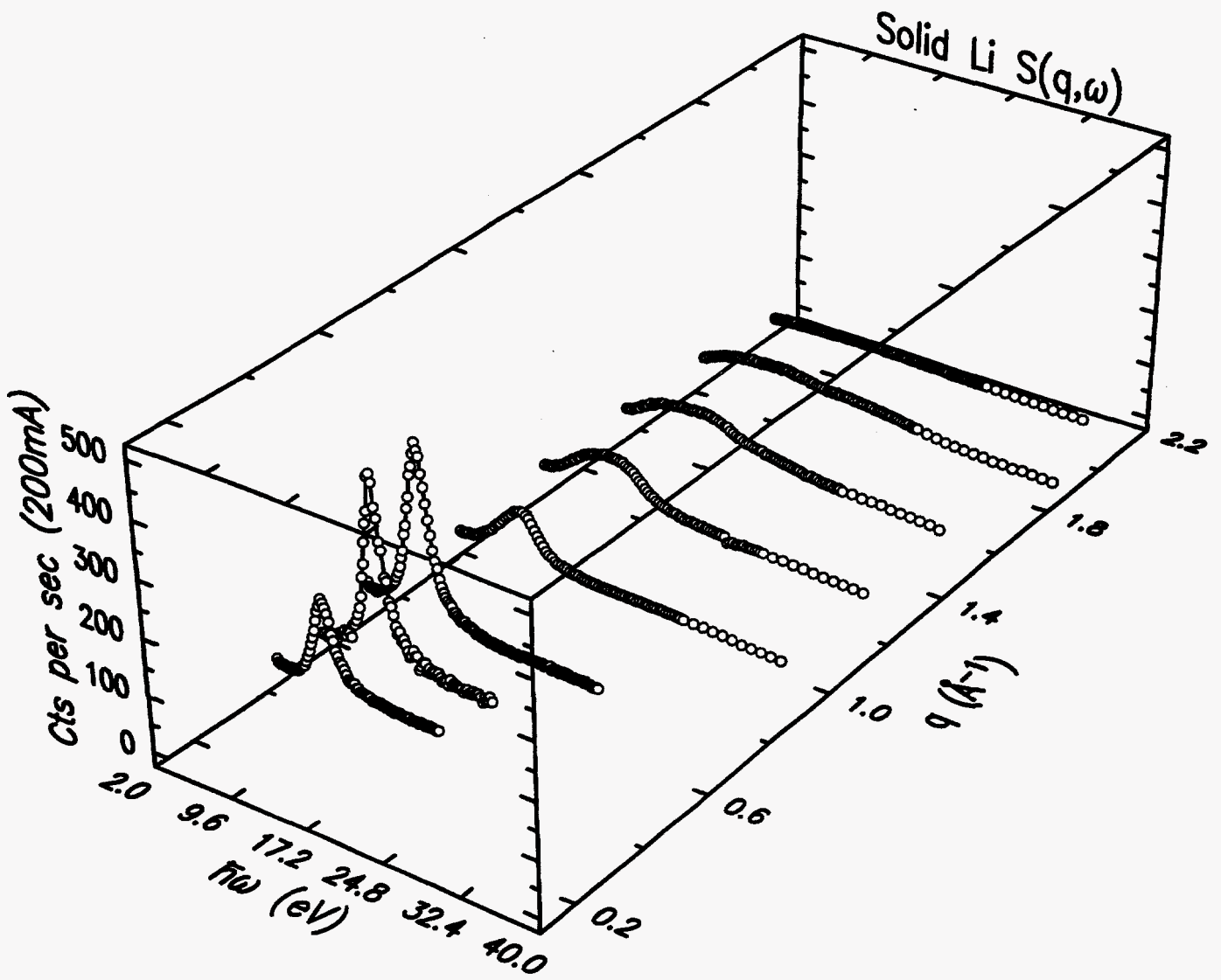


Figure 2: Dynamic structure factor of Li as measured by x rays.

in order to maintain the backscattering condition on the analyzer. Scans are performed at fixed q . The overall energy resolution of the spectrometer was 0.5 eV (HWHM), dominated by source size contributions.

The experiments were performed in transmission, with the sample thickness chosen to be approximately twice the x-ray absorption length, to maximize the inelastic signal.

4 Simple Metals

Simple metals, i.e. those that may be described by the nearly-free-electron model, have long been a test case for theories of electron behavior in solid state systems. Early x-ray experiments on such systems by Platzman, Eisenberger, Schülke and others [4, 5, 6, 7, 8] revealed discrepancies with the predictions of the RPA, as summarized in figs. 3 and 4.

The deviations take the form of a shift to lower energies of the peak position, and a reversal of the asymmetry of the overall shape of the response. In addition, there is fine structure in the response, which is entirely absent in the RPA calculation. As discovered by Schülke *et al.* [7], some of the fine structure is orientation-*dependent* (bottom two panels fig 3), and is therefore associated with band structure-induced transitions (which are not included within the jellium RPA). Nevertheless, even in powder samples (top panel), there remained some orientation-*independent* fine structure, which was not understood. While some theoretical work suggested that it arose from many-body effects (that is higher order corrections to the RPA, which is strictly only valid for $r_s \ll 1$) (eg. ref. [9]), others suggested that this structure also arose from band structure effects [10].

The purpose of our recent work [11], was to empirically distinguish between these two explanations and determine the role of the long range order, both for the orientation-independent fine structure and the overall shape of the response function. We carried out a comparison of data taken in the liquid and solid phase of three metals; Li, which is believed to have strong band structure effects, Na, which had not previously been studied in this regime, and Al, which is believed to be most nearly-free-electron-like. A comparison of the liquid and solid response for Li is shown in fig. 4 with data taken above and below the melting temperature. The overall shape of the response is unchanged on melting, proving that this is not determined by the long

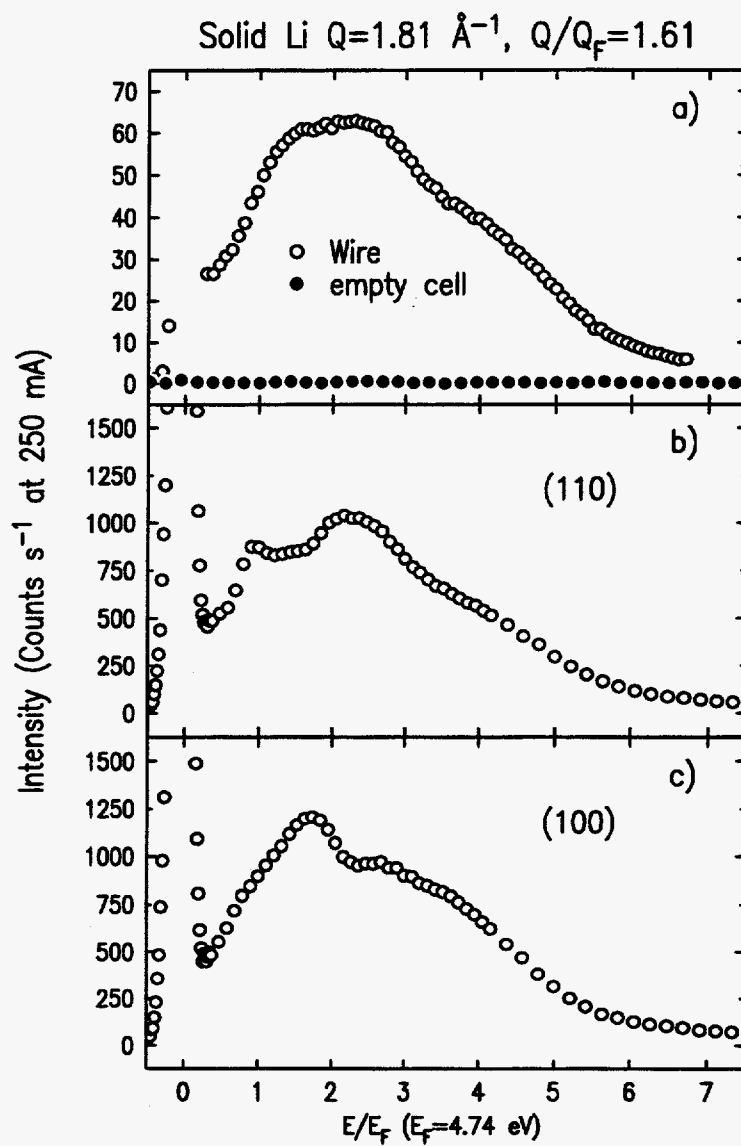


Figure 3: Energy scans at $Q=1.81 \text{ \AA}^{-1} = 1.61 k_F$ in solid lithium. a) data taken on polycrystalline wire. Closed circles show empty cell scan. Single crystal data with b) \vec{q} parallel to (110) c) \vec{q} parallel to (100)

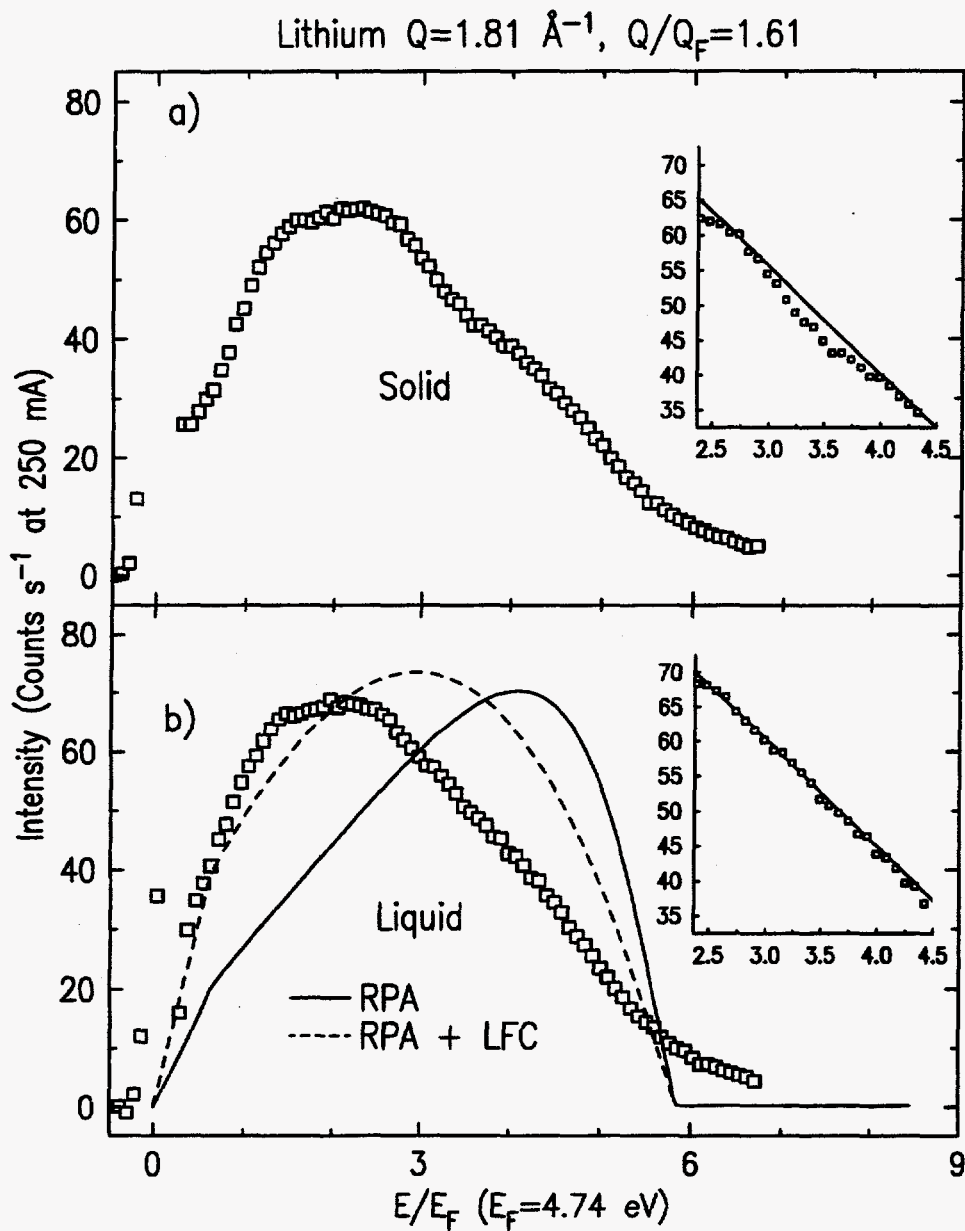


Figure 4: Lithium data at $Q=1.81 \text{ \AA}^{-1}$ (a) below and (b) above the melting temperature. Insets display the 12-20 eV region with a straight line guide to the eye of the same slope. Solid line in (b) is the RPA prediction and the dashed line the effect of a local field correction.

range order. Conversely, the fine structure present in the solid phase (insets) disappears on melting, demonstrating unambiguously that it is associated with the long range order, and is not a many body effect as had previously been claimed.

While short range ionic correlations still exist, these liquid phase data allow, for the first time, a comparison with theories of the homogeneous electron gas without the complication of long range periodicity effects. We begin with the RPA dielectric function. The short range effects of exchange and correlation are approximated by the static local field correction $g(q)$ of Ichimaru and Utsumi [12], modifying the dielectric function according to

$$\epsilon(\vec{q}, \omega) = 1 + \frac{\epsilon^{\text{RPA}}(\vec{q}, \omega) - 1}{1 - g(q)(\epsilon^{\text{RPA}}(\vec{q}, \omega) - 1)}. \quad (4)$$

The unmodified RPA result is shown as a solid line in fig. 4b. The peak energy and asymmetry of the calculated response are badly wrong. The local field correction of ref [12] (dashed line) improves the agreement, but is not sufficient. Inclusion of a finite electron lifetime, or a dynamic local field correction $g(q, \omega)$, further improves the agreement but requires a judgement of the relative merit of the various theoretical approaches which is beyond the scope of this paper.

In Fig. 5, we show the corresponding data for solid and liquid sodium ($k_F = 0.92\text{\AA}^{-1}$). These data were taken at $q = 1.46\text{\AA}^{-1} = 1.6k_F$; the same scaled momentum transfer as in fig. 4. As before, the solid phase data represent a powder average of any orientation-dependent effects and the quasi-elastic response has been subtracted. Sodium is more free-electron-like and indeed to within our experimental statistics, no fine structure is evident in the solid phase data. The liquid phase data are essentially identical to the solid phase, consistent with a negligible influence of long range periodicity band structure effects, to within errors. As before, the local field correction improves agreement between theory and experiment, but is not sufficient.

Following on from this work, we turned to Al, which displays strong orientation-independent fine structure, despite the fact that band structure effects were believed by some to be negligible. Preliminary studies of liquid Al reveal that even in this case, the fine structure is damped or removed in the liquid phase and that it is therefore a consequence of the long range order.

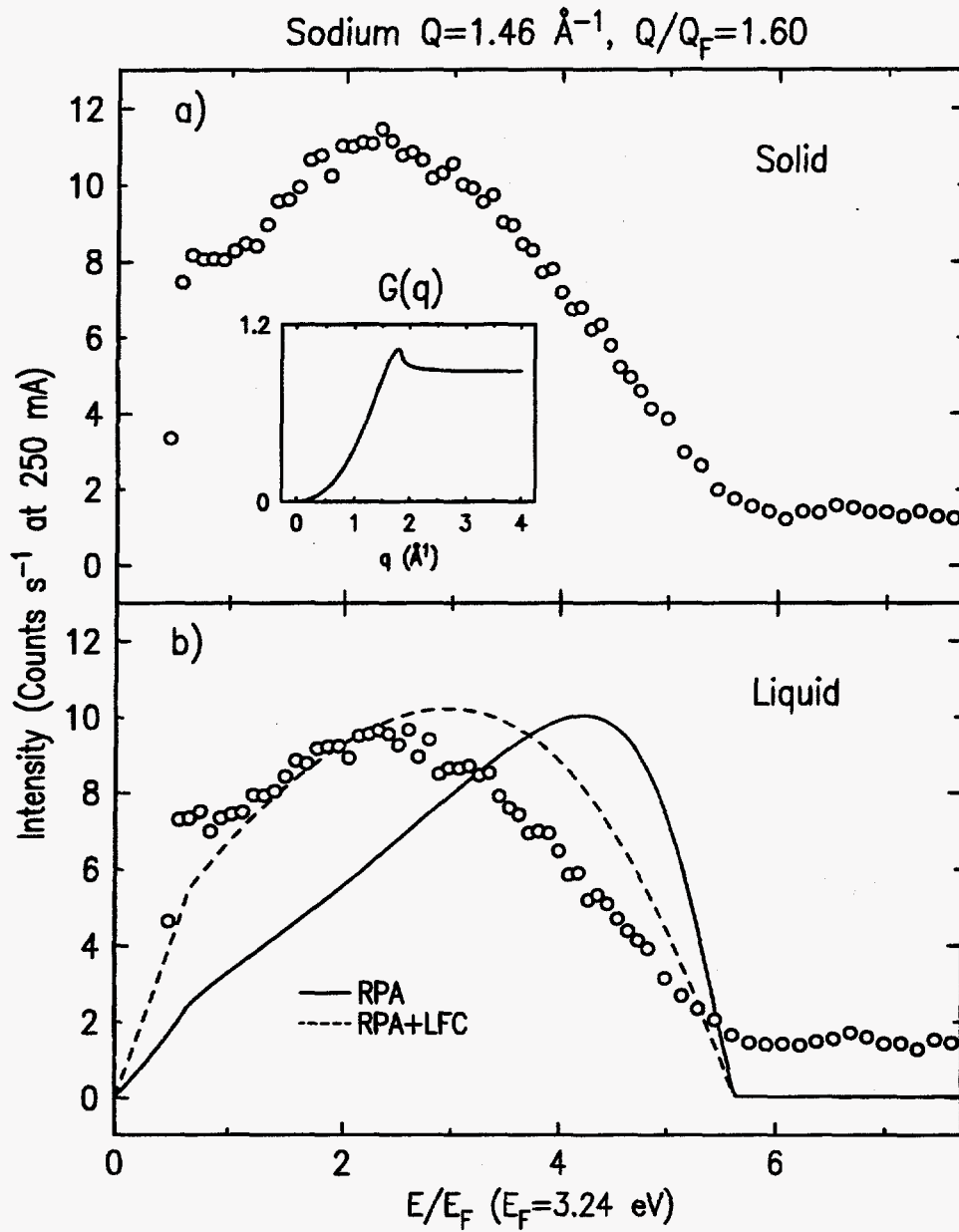


Figure 5: Sodium data at $Q=1.46 \text{ \AA}^{-1}$ (a) below and (b) above the melting temperature. Inset is the local field correction used for Na. Solid and dashed lines as fig. 4

In summary, it is clear that many body effects are not responsible for the fine structure observed in the single particle excitation spectrum of metals. This in turn places constraints on the corrections to the RPA which the liquid data still demand.

We now turn to the small q response, which is dominated by the collective excitations. It is known from electron scattering results that deviations from RPA also occur in this regime [13]. In Fig. 6a), the plasmon dispersion is shown as obtained in solid and liquid lithium. The predictions of the RPA and the local field corrected RPA are also shown. Within the RPA, plasmon dispersion is expected to be approximately quadratic, $E_p(q) = E_p(0)(1 + \alpha(\hbar^2/m)q^2)$ where $\alpha^{\text{RPA}}(\text{Li}) = 0.34$. For solid lithium we find $E_p^{\text{solid}}(0) = 7.31 \pm 0.06\text{eV}$ and $\alpha_{\text{solid}} = 0.18 \pm 0.04$, in reasonable agreement with electron scattering data, $\alpha_{\text{EELS}} = 0.24 \pm 0.04$ [13]. These numbers are well below the RPA values and this has been attributed to the influence of inter-band transitions [14]. On melting, there is a decrease in the $q = 0$ plasmon frequency to $E_p^{\text{liquid}}(0) = 7.12 \pm 0.03\text{eV}$ and we find $\alpha_{\text{liquid}} = 0.19 \pm 0.04$. To within errors, the plasmon dispersion is unchanged. The shift in plasmon frequency is entirely explained by the reduction in electron density on melting.

In Fig. 4b, the half-width of the plasmon loss, obtained from a Lorentzian fit, is plotted for both the liquid and solid phase data. For all q the peaks are broader than the resolution, that is, the plasmon has a finite lifetime. A number of non-RPA mechanisms are believed to be responsible for plasmon decay [15, 16], the dominant of which are interband transitions and phonon-assisted interband transitions.

The explanations for the non-RPA behavior of the plasmons require inter-band transitions and yet no change is seen in the plasmon data on melting. We therefore conclude that the short range ionic correlations of the liquid are sufficient to mimic the packing arrangement of the solid [17] and, on the length scale probed by the plasmons (1-10Å), determine the electronic properties i.e, an effective band structure is set up. Such a conclusion has in fact been reached previously, on the basis of NMR results [18]. Indeed, interband transitions in liquid aluminum have been observed in optical measurements [19] and electron scattering measurements of the plasmon dispersion in solid and liquid gallium and tin found no change on melting, though in these cases the lifetime was observed to change [20]. Also theoretically, similar ideas have met with some success [21]. In contrast, the single particle excitation

Plasmons in Lithium

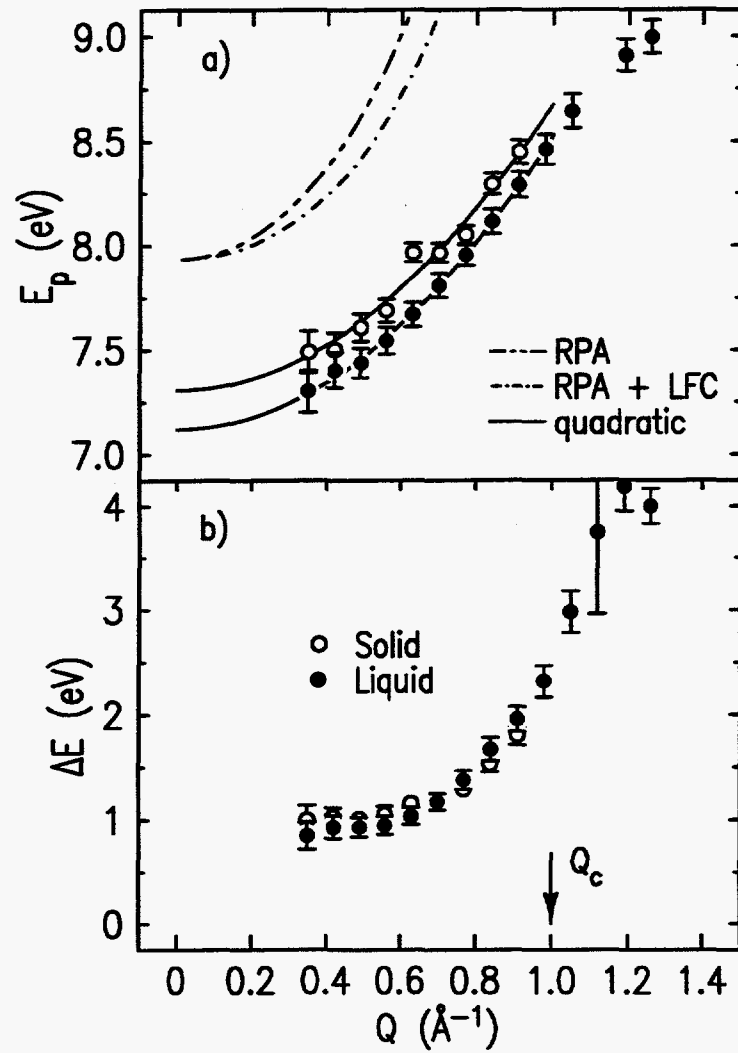


Figure 6: (a) Dispersion of plasmon frequency. (b) Plasmon lifetime, in solid and liquid

spectrum is sensitive to the long range periodicity due to the delocalized nature of the valence electrons.

5 Other Systems

The use of inelastic x-ray scattering in the study of condensed matter systems is growing rapidly in both the meV and eV regimes, and it would be difficult to provide a comprehensive survey of the field. Rather, the purpose of this section is to give a flavor for the work that has been done to date in the study of electronic excitations.

Other than a large body of work on the dynamic response function of simple metals, studies of electron dynamics have been carried out on solid He [22] and single crystal C_{60} [23]. Also band structure studies have been performed on pyrolytic graphite [24] and diamond [25]. In addition the metal-antiferromagnetic insulator transition has been studied in the Mott-Hubbard system V_2O_3 [26]. Other systems investigated include TiC and Ti [27]. We have also carried out studies of mesoscopic systems, including Al clusters and carbon nanotubes [28]. The dispersion of the π and $\sigma + \pi$ plasmons in the latter are shown in fig. 7.

Perhaps the most intriguing development in this area is the discovery of resonant enhancements in the inelastic cross-section on tuning the incident photon energy through an atomic absorption edge. (This scattering arises from the $\vec{A} \cdot \vec{P}$ terms in the interaction Hamiltonian and was not included in equations 1 and 2). The first observation of such an enhancement was in the work of Kao *et al.* in NiO [29]. These workers observed a charge transfer excitation only in the vicinity of the Ni K-edge, and estimated the enhancement factor to be ~ 100 . Similar effects have also been seen in Nd_2CuO_4 at the Cu K-edge [28]. Such enhancements offer the possibility of extending the applicability of inelastic x-ray scattering to materials with relatively large absorption, and are therefore of great current interest.

6 Conclusion

Inelastic x-ray scattering measures the charge fluctuation spectrum over large regions of (q, ω) space. In many ways complementary to existing inelastic

Carbon Nanotubes

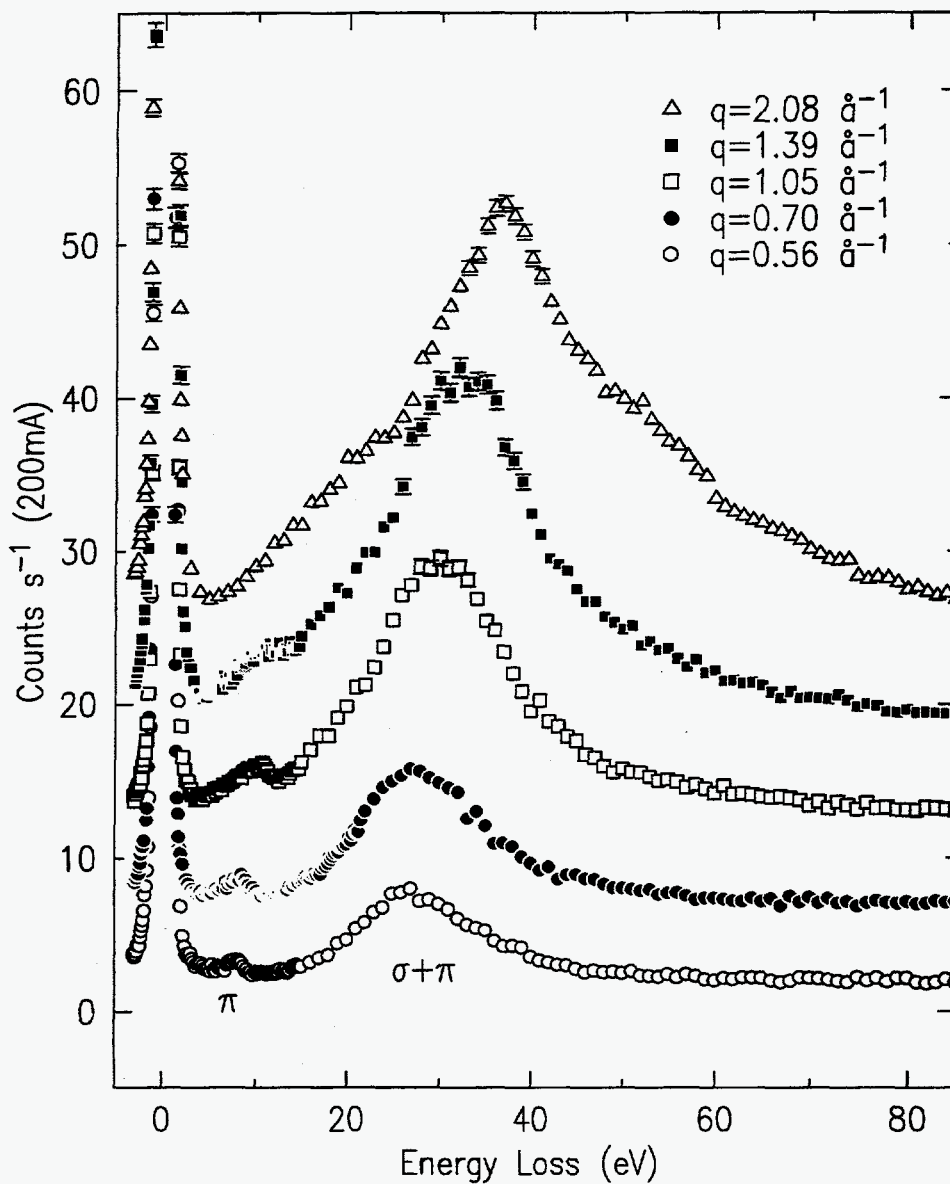


Figure 7: Energy loss spectra from carbon nanotubes. These are cylindrical carbon structures, $\sim 1\mu\text{m}$ long and $\sim 10\text{\AA}$ in diameter. Two plasmon-like excitations are visible.

scattering techniques, it offers a new tool for the experimental condensed matter physicist. While the technique is still in its relative infancy, the development of dedicated beamlines at a number of synchrotrons is having a large impact on the field. In particular, so called third generation sources are especially well suited to high energy resolution beamlines and the field is expected to grow rapidly in the coming years.

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