

Inelastic X-Ray Scattering Study of Solid and Liquid Li and Na

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We present the first measurements of the dynamic structure factor of lithium and sodium in the liquid and solid phases, in the intermediate- q regime. The overall shape of the response function is little changed on melting, implying that it is not determined by the long range order of the ion cores. Conversely, fine structure, observed in the Li data, disappears on melting, and is attributed to band-structure-induced transitions. At small q , the plasmon lifetime and dispersion remain unchanged on melting. [S0031-9007(96)01462-7]

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The homogeneous electron gas is one of the oldest and most studied many-body problems in solid state physics. Its properties, as described by the complex dielectric function $\epsilon(\mathbf{q}, \omega)$, were first calculated by Lindhard in the random phase approximation (RPA), valid at high densities. Subsequent approaches [1] have modified the RPA by attempting to include the effects of the exchange and correlation hole with a so-called local field correction $g(\mathbf{q})$. Numerous local field corrections have appeared in the literature. Experimentally, scattering techniques measure the dynamic structure factor, which is related to the dielectric function through the fluctuation dissipation theorem [2],

$$S(\mathbf{q}, \omega) = -\frac{\hbar q^2}{4\pi^2 e^2 n} \text{Im} \epsilon^{-1}(\mathbf{q}, \omega). \quad (1)$$

However, traditional scattering techniques have limitations in this endeavor. These include neutron scattering, which does not couple directly to the electrons, and light scattering, which cannot obtain the required momentum transfers. Electron scattering has been successful at small momentum transfers [3] but suffers from multiple scattering effects at higher q , making the spectra difficult to interpret. It is also surface sensitive, an inconvenience in the study of bulk properties.

As first realized in pioneering work by Platzman and Eisenberger, and Schülke and co-workers, inelastic x-ray scattering offers a unique tool for studying the full dynamic response function of the electron gas. A weakly interacting probe, it suffers from none of the above limitations and the cross section is simply interpretable for all momentum transfers.

Early experiments on simple metals showed discrepancies with the RPA predictions in the intermediate- q regime, both in the overall shape of the response and its position, which is shifted to lower energies. In addition, fine structure in the form of a double peak-type response was observed. These features appeared to be universal and were attributed to many-body corrections to the RPA [4]. Indeed, theoretical support for this view was forthcoming [5]. Subsequent work on single crys-

tals, however, highlighted the orientational dependence of some of the fine structure and emphasized the role of the electron-ion interaction and band structure effects [6]. Using pseudopotential schemes some of these features could be reproduced. However, there remains orientation-independent fine structure whose origin has not yet been clearly identified. The experiments have stimulated recent attempts at *ab initio* calculations of $S(\mathbf{q}, \omega)$ [7]. Given the complexity of the various theoretical approaches, it is important to have an experimental, model-independent determination of the origins of the deviations from the RPA.

The purpose of this work is twofold: firstly, to ascertain the origin of the fine structure observed in the intermediate- q regime by melting lithium and sodium and removing the long range ordered periodic potential of the ion cores, and secondly, to use the liquid phase data as a closer approximation to the jellium models of most theories, which do not include the effects of long range order, for a more realistic test of these theories. We discuss both the plasmon excitation at small q and the single particle excitations at intermediate q . We find that in the intermediate- q regime, the fine structure observed in the solid phase Li data is not present in the liquid data and is therefore attributed to the long range periodicity. We find no fine structure in the solid sodium data. At small q , deviations in the plasmon dispersion and frequency from the RPA values are found to be unchanged on melting. We speculate that the short range order of the liquid is sufficient to allow "interband-like" transitions within some effective band structure.

The alkalis are particularly simple metals, with a single free-electron-like valence electron. Lithium ($r_s = 3.27$) was chosen for this work because it gives rise to a large x-ray inelastic signal. Also, the response in the solid phase has been previously characterized with inelastic x-ray scattering [6,8] and band structure effects are believed to be important (requiring relatively large pseudopotential coefficients). It melts at $T_M(\text{Li}) = 453$ K. Sodium ($r_s = 3.93$) represents a useful foil to the Li results. It is more free-electron-like and has not been

studied previously by inelastic x-ray scattering techniques. $T_M(\text{Na}) = 371$ K. This work was carried out at beamline X21, at the National Synchrotron Light Source. A horizontally focusing, miscut Si(220) monochromator was utilized with a spherically bent Si(444) analyzer [9]. The energy resolution was ≈ 0.7 eV FWHM. The experiments were performed in transmission.

For the lithium work, a polycrystalline wire of diameter 4 mm was placed in a stainless steel holder between two 0.05 mm thick Be windows. In the liquid phase, surface tension was sufficient to retain the shape of the wire. The Be windows produced no measurable scattering with appropriately set slits. For the Na experiments, the Na was placed in a thin-walled (0.01 mm) glass capillary of diameter 0.6 mm sealed under a He atmosphere. There was a negligible inelastic signal from the glass. The sample appeared silvery both before and after data taking. The sample cells were each then placed in an evacuated outer can with mylar windows to reduce the background due to air scattering.

The Li response at $q = 1.81 \text{ \AA}^{-1}$ ($= 1.61k_F$, $k_F = 1.12 \text{ \AA}^{-1}$), is shown in Fig. 1. Here the single particle excitation spectrum is probed. The statistical error bars are smaller than the points. In Fig. 1(a), data from the wire sample are shown (open circles) together with the empty cell background (closed circles). Although this is a powder sample and band structure effects are

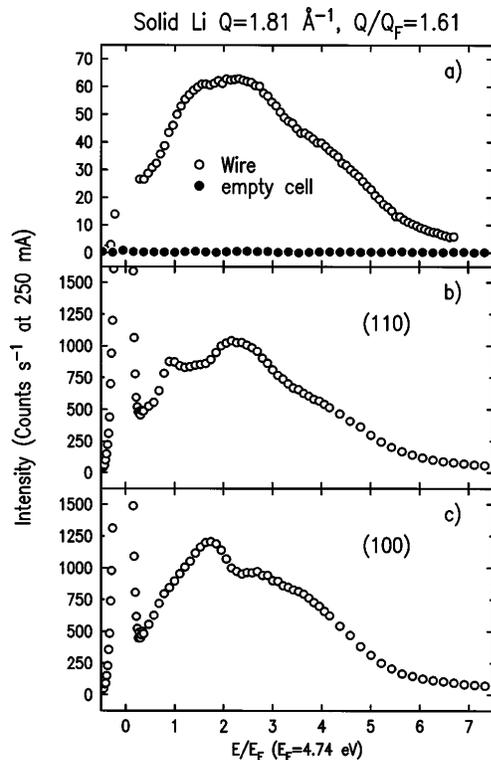


FIG. 1. Energy scans at $|\mathbf{q}| = 1.81 \text{ \AA}^{-1} = 1.61k_F$ in solid lithium. (a) Data taken on the wire (polycrystalline). Closed circles show an empty cell scan. Single crystal data with (b) \mathbf{q} parallel to (110) and (c) \mathbf{q} parallel to (100).

orientationally averaged, there is still some fine structure evident in the shoulder of the spectra at $\sim 3.6E_f$ (17 eV). In addition, the overall shape of the spectra is distinctly non-RPA-like. It is these aspects of the response function that we wish to investigate on melting. In Figs. 1(b) and 1(c) we show spectra taken on a single crystal of Li, at the same momentum transfer, in two different directions [10]. These spectra show dramatic orientation-dependent fine structure and are in quantitative agreement with single crystal data of Schülke *et al.* [6]. These authors have interpreted the peaks of the (110) spectrum at $\sim E_f$ (5 eV), and of the (100) spectrum at $1.7E_f$ (8 eV), as arising from excitation gaps opened by the presence of the (110) and (200) Bragg planes, respectively. These are the so-called zone boundary collective states of Foo and Hopfield [11]. However, the peak in the (110) spectrum at $2.3E_f$ (11 eV), and the dip at $3.6E_f$ (17 eV), both of which survive in the powder averaged data, Fig. 1(a), were less clearly identified with band-structure-induced effects.

A comparison of data taken in the solid and the liquid phases is shown in Fig. 2. The quasielastic line has been subtracted off these data. This was achieved by fitting the energy gain side of the elastic line and subtracting a symmetrized version of the line shape. Because of uncertainties in this procedure, data points below 3 eV

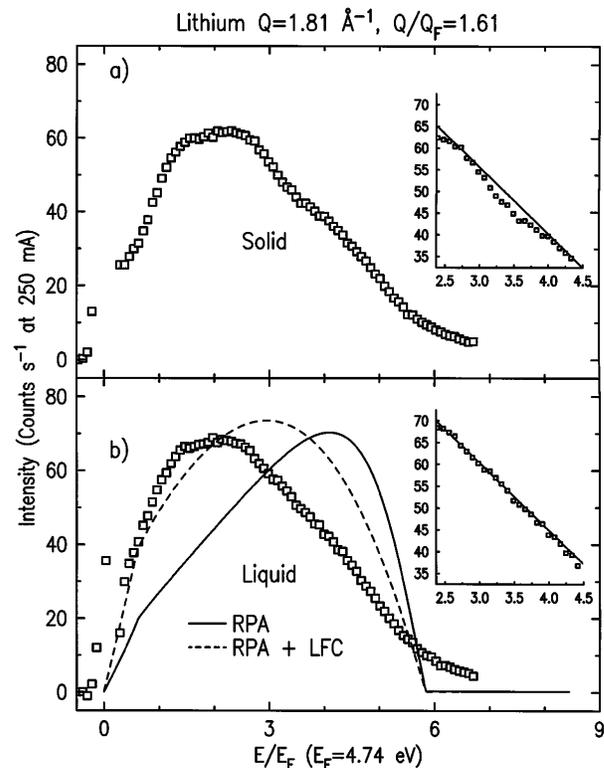


FIG. 2. Lithium data at $|\mathbf{q}| = 1.81 \text{ \AA}^{-1}$ (a) below and (b) above the melting temperature. Insets display the 12–20 eV region with a straight line guide to the eye of the same slope. Solid line in (b) is the RPA prediction and the dashed line the effect of a local field correction.

are less reliable. The insets detail the region of energy transfer from $2.5E_f$ to $4.5E_f$. The solid lines are straight line guides to the eye. The dip at $3.6E_f$ is clearly visible in the solid phase data, but is entirely absent in the liquid phase, demonstrating that it is associated with the long range periodic potential of the ion cores and is *not* a feature of the homogeneous electron gas.

In contrast, the overall shape and peak position of the spectra, both of which deviate sharply from the RPA prediction, do not change on melting. One may now apply the machinery for calculating $\epsilon(\mathbf{q}, \omega)$ for a homogeneous system to the liquid phase data. While short range ionic correlations still exist, these data allow, for the first time, for comparison with theories of the homogeneous electron gas without long range periodicity effects. We begin with the RPA dielectric function. The 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

$$\epsilon(\mathbf{q}, \omega) = 1 + \frac{\epsilon^{\text{RPA}}(\mathbf{q}, \omega) - 1}{1 - g(q)[\epsilon^{\text{RPA}}(\mathbf{q}, \omega) - 1]}. \quad (2)$$

The form of $g(q)$, calculated for sodium, is shown in the inset of Fig. 3(a). The unmodified RPA result is shown as a solid line in Fig. 2(b). The peak energy and asymmetry of the calculated response are badly wrong. The local field correction of Ref. [12] (dashed line)

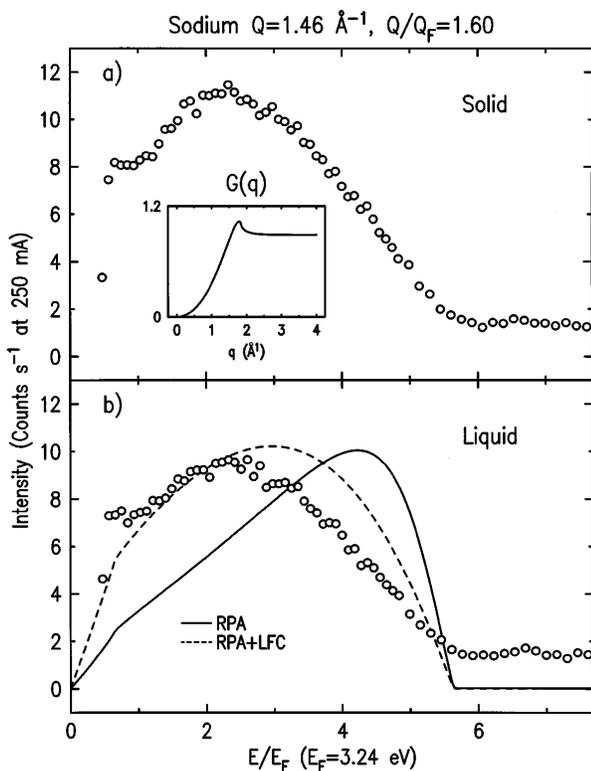


FIG. 3. Sodium data at $|\mathbf{q}| = 1.46 \text{ \AA}^{-1}$ (a) below and (b) above the melting temperature. Inset in (a) is the local field correction used for sodium. Solid and dashed lines as Fig. 3.

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 judgment of the relative merit of various theoretical approximations, which violates the spirit of the present work. Rather, it is hoped that the liquid phase data will provide workers a means to test various approaches without the complication of a long range periodic potential.

In Fig. 3, 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. 2. As before, the solid phase data represent a powder average of any orientation-dependent effects and the quasielastic 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.

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 [3]. In Fig. 4(a), 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

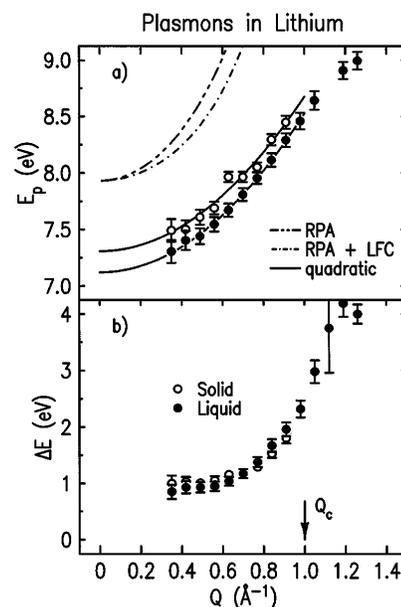


FIG. 4. (a) Dispersion of plasmon frequency. (b) Plasmon lifetime, in solid and liquid Li.

electron scattering data, $\alpha_{EELS} = 0.24 \pm 0.04$ [3]. These numbers are well below the RPA values and this has been attributed to the influence of interband transitions [13]. On melting, there is a decrease in the $q = 0$ plasmon frequency to $E_P^{\text{liquid}}(0) = 7.12 \pm 0.03$ 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. 4(b), 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 [14,15], the dominant of which are interband transitions and phonon-assisted interband transitions.

The explanations for the non-RPA behavior of the plasmons require interband 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 [16] and, on the length scale probed by the plasmons (1–10 Å), 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 [17]. Indeed, interband transitions in liquid aluminum have been observed in optical measurements [18] 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 [19]. Also theoretically, similar ideas have met with some success [20]. In contrast, the single particle excitation spectrum is sensitive to the long range periodicity due to the delocalized nature of the valence electrons.

In summary, we have used inelastic x-ray scattering to measure the dielectric response function of lithium and sodium in the liquid and solid phase. In the case of lithium, some fine structure present in the spectrum at intermediate wave vectors disappears on melting. This is attributed to the presence of band-structure-induced transitions due to the long range order of the solid phase. In sodium, the influence of band structure is not evident in our data. By comparison of the liquid phase data to modified RPA theories, we find a static local field correction improves agreement but the magnitude of the required correction appears to be larger than current theories obtain. For the plasmons the effect of melting is small. This suggests that the short range order present in the liquid generates an effective band structure, on the length scale relevant to the plasmons, which modifies the plasmon response due to inter-“band” transitions.

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