X-Ray Inelastic Scattering of Li Metal

P. Eisenberger, P. M. Platzman, and P. Schmidt
Bell Laboratories, Murray Hill, New Jersey 07974
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X-ray inelastic scattering experiments performed on bare Li metal in a vacuum do not reveal any L-x-ray Raman band as has been previously reported. The Li results reported here are similar to those observed in other materials.

In a recently reported inelastic x-ray scattering study[1] of Li a new component was observed in the scattering spectrum centered near $E/E_F = 1$, where $E_F = 4.7$ eV is the Fermi energy for Li. This component was called by the authors an L-x-ray Raman band. In this work we report the results of similar studies on Li. However, in addition to studying Li in air with an oil-Mylar cover to prevent oxidation (as was used in Ref. 1), we have also studied bare Li in a vacuum as well as the oil-Mylar cover with no Li at all. Our studies of Li in air with the protective cover give very similar results to those reported by other authors[1] and will not be reproduced here. Our results for bare Li in a vacuum do not reveal any L-x-ray Raman band feature but our studies of the oil-Mylar cover do show a peak in the scattered spectrum at an energy of approximately 5 eV.

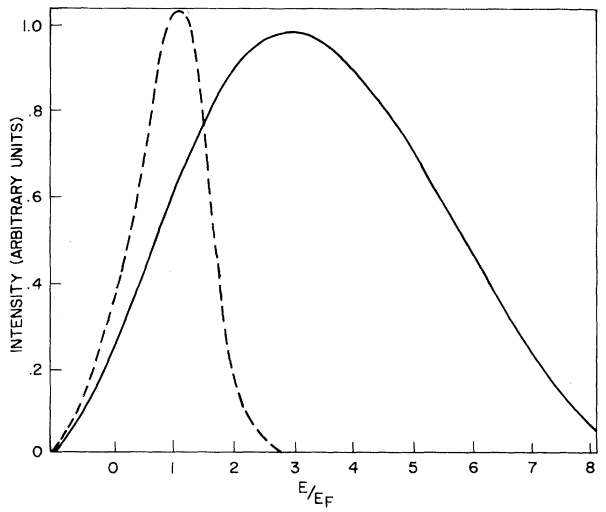

FIG. 1. The scattering spectrum at momentum transfer $k/k_F = 1.77$ ($k_F = 1.1$ Å^{-1}) for bare Li in a vacuum (solid line) and for the oil-Mylar cover (dotted line). The oil-Mylar spectrum was not investigated beyond 15 eV and preliminary studies indicate it is the Mylar not the oil which is mainly responsible for the feature observed at 5 eV.

The experimental technique and data processing are identical to those previously reported.[2,3] In Fig. 1 the solid line is the spectrum for bare Li measured in vacuum at a momentum transfer of $k/k_F = 1.77$. The vacuum measurements of Li were performed on a freshly cleaned piece of Li which was placed in a vacuum chamber whose windows were not in the scattering volume. This latter fact was substantiated by performing an experiment in which no signal was observed when there was no sample in the chamber. The Li sample was examined after the measurements and found not to have acquired any appreciable oxide coating (thickness less than 0.1 μm). The dotted line is the spectrum measured for the oil-Mylar cover at the same scattering angle. The intensities as pictured in Fig. 1 are arbitrary, though to within experimental error of $\pm 10\%$ the sum of the spectra of bare lithium plus the oil-Mylar cover was equal to the spectrum of lithium with the oil-Mylar cover measured in air. The similarity of the composite spectrum with that reported in Ref. 1 is striking. As mentioned above, studies of Li with an oil-Mylar cover at other scattering angles revealed the same spectra and intensity dependences observed in Ref. 1. This resemblance together with the knowledge that an oil-Mylar protective cover[4] was used in the previous work clearly leads one to the conclusion that the feature at $E/E_F = 1$ is not an L-x-ray Raman band from Li but is actually a property of the oil-Mylar protective cover.

The spectra of single-crystal Li measured in a vacuum, for several values of the momentum transfer k, are shown in Fig. 2. These measurements were made for k along the $\langle 110 \rangle$ or $\langle 211 \rangle$ directions, and no appreciable anisotropy was observed. This observation is in accord with theoretical ideas which predict that at low momentum transfers the lowest-order contribution to the anisotropy is zero in cubic systems.[5]

In earlier experiments[2,3] on Be, Al, and graphite we observed a spectrum that was dominated at low momentum transfer by a relatively sharp

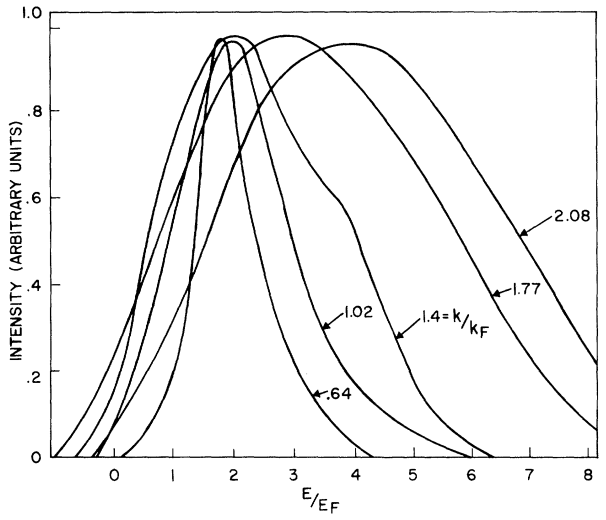

FIG. 2. The scattering spectra for bare single-crystal Li measured in a vacuum at several values of momentum transfer. The observed spectra were identical with the momentum transfer in either the [110] or [211] direction.

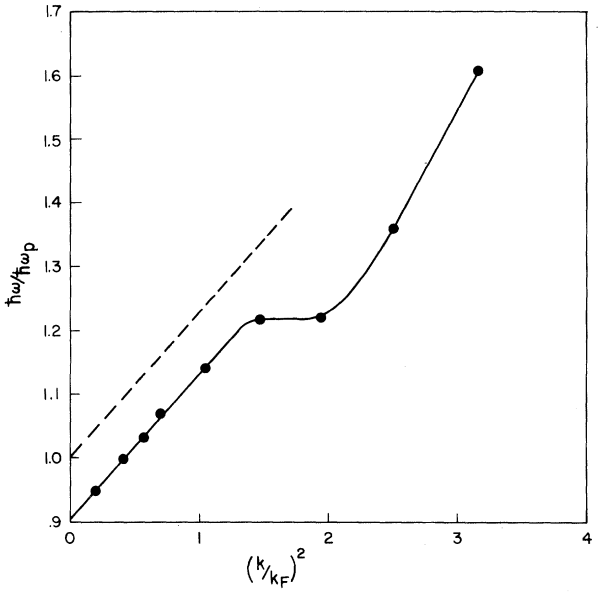

FIG. 3. The peak of the Li spectra is plotted in units of the $k=0$ free-electron plasmon value of 8.050 eV as a function of the square of momentum transfer in units of the Fermi momentum $k_F = 1.1$ Å^{-1}. The experimentally deduced $k=0$ value is 7.2 eV.

plasmonlike excitation. At intermediate momentum transfers ($1 > k/k_F < 2$) the spectrum split into two quite distinct portions: (1) A relatively nondispersive (k-independent) plasmonlike peak persisted in disagreement with the predictions of simple random-phase-approximation (RPA) theory. (2) A broad portion of the spectrum centered around $k^2/2m$ grew in intensity and ultimately dominated the entire spectrum.

In Li this split spectrum is not as prominently displayed. The data, however, are consistent with such a picture. The spectrum taken at $k/k_F = 1.4$ clearly shows a peak sitting on a broad underlying background. The data at other momentum transfers do not show this effect clearly. The reason for this is simply that the widths of the collective modes, which arise primarily from band-structure effects, are roughly constant in energy as, for example, one goes from Li to Be. Thus, relatively speaking the collective mode structure in Li is much broader than its counterpart in a material like Be (i.e., we cannot resolve the two features in Li).

A plot of the peak portions of the spectrum (Fig. 3) reveals the essential behavior. At long wavelengths the broad collective mode has a $k=0$ value which is $\cong 0.9(\hbar\omega_p)_{\text{free}}$. It disperses roughly like αk^2 where the coefficient α is quite comparable to its RPA value,

$$\alpha = 0.3\omega_p(k^2/k_F{}^2).$$

These results are in agreement with those obtained by electron scattering.[6] For $1 < k/k_F < 2$ the flattening of the dispersion signals the breakup of the spectrum while for $k/k_F > 2$ the position is roughly consistent with the RPA result.

It is clear that the data on Li are further proof of the universality of the effects reported earlier. The exact cause of these striking deviations from RPA are still unknown. Our previous speculations[6,7] as to its origin concerned themselves with the effect of short-range correlations in the electron gas. It seemed to us that the persistent nondispersive characteristic associated with the excitation of a single electron trapped in a potential well was a useful characterization of the spectrum. The additional possibility that multiple-pair-plasmon final states can lead to such effects has arisen. In such a situation a recoiling electron virtually scatters off the electron gases creating a well-defined plasmon of low momentum. The simplest model of such a process leads one, because of kinematics, to the conclusion that the spectral weight for this process lies in the neighborhood of $\hbar\omega_p + k^2/2m^*$. Some mechanism by which the recoiling electron gives its momentum to the gas as a whole must be found if one is to reconcile such a process

with the observed data.

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Sharp Optical Spectra of Impurities in Metals*

R. A. Tilton† and C. P. Flynn
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801
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We report sharp optical absorption spectra, lacking evidence of carrier-pair creation process, for both like and unlike rare-gas atom pairs in alkali metals. The excited molecular orbital is probably a virtual bound state. These pair spectra also provide insight into optical properties of solid rare gases.

Optical excitation spectra of local centers in metals usually have threshold edges with continuum absorption extending for many eV on the high-energy side.[1] The lack of sharp, symmetrical absorption lines has been attributed to the electron-hole pair-creation process occurring in the recoil of the Fermi liquid to its self-consistent excited configuration.[2] These are, for example, the characteristics of both host and impurity core excitations in metals when the hole is effectively localized on one lattice site. In this paper we report the first observation of sharp impurity spectra lacking free-carrier creation processes. The sharp lines are identified unambiguously as arising from pairs of rare-gas atoms in alkali metal hosts. In width and location they resemble the exciton lines observed in rare-gas solids. Their emergence in metallic hosts undoubtedly indicates that the excited diatomic molecular orbital exists as a virtual or bound level coupling weakly with the host electron gas.

Figure 1(a) shows for various Xe concentrations c (at.%) the logarithm of the absorption *per impurity atom* by Xe impurities in K at 7°K. The experiments determined the loss of transmission, using methods described elsewhere.[3] Very similar results have been obtained for Xe and for Kr in all the alkali metals. In each case sharp lines emerge with increasing impurity concentration. The observed peaks are extraordinarily sharp (~ 200 meV full width) and symmetrical for metals. A different pattern of lines emerges in Fig. 1(b), which shows the impurity absorption when various concentrations of Ar are added to K containing ~ 2-at.% Xe.

The origins of the sharp structure are clarified by Figs. 2(a) and 2(b), which show the peak heights as functions of impurity concentrations c_{Xe} and c_{Ar}. In Fig. 2(a) the height of the peak in Fig. 1(a) is shown to depend linearly on c_{Xe}. As Fig. 1(a) depicts the absorption per Xe atom, Fig. 2(a) shows that the peak height rises in proportion to the probability with which sites neighboring each Xe are occupied by Xe atoms. In Fig. 2(b) the incremental heights of the absorption peaks for K containing both Xe and Ar [see, e.g., Fig. 1(b)] are shown to depend linearly on the product $c_{Xe}c_{Ar}$ of the impurity concentrations. For random distributions of species among sites in the alloys, the results of Fig. 2(a) establish unambiguously that the sharp peaks in Fig. 1(a) are associated with two Xe atoms occupying neighboring sites. Similarly, the results of Fig. 2(b) show that the peaks in Fig. 1(b) are associated with Xe-Ar pairs. The random nature of the alloys is established in the following paper[3] concerning the metal-insulator transition.

Figures 1 and 2 also indicate that nearest-neighboring rare-gas atoms in metals maintain two (or more) competing excitation channels that combine to keep the total oscillator strength approximately constant (as indicated by the areas under the curves in Fig. 1). This follows from the fact that a channel blurred by electron and hole creation processes is unlikely to produce