tion is derived. Our results cannot be explained within the framework of this approach, firstly, because we observe a strong $T^{3/2}$ dependence in a doped cubic metal where it is difficult to assume such an interaction; secondly, because we observe a correlation between the intensity of the quadrupole nuclear interaction and the strength of the temperature variation, characterized by the coefficient α, which is opposite to what should be expected in the proposed model.

We would like to add that the low-frequency distributions also display a temperature-dependent variation but because the errors are large we are not extracting definite conclusions.

In summary the present experimental results show that in a cubic metal doped with impurity a $T^{3/2}$ relation for the EFG is also observed and that the slope of this temperature dependence strongly depends on the valence and/or mass of the impurity.

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*Work supported by Financiadora de Estudos e Projetos and Conselho Nacional de Desenvolvimento Científico e Technológico, Brasil.

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Electronic Excitations in LiF: 10–70 eV*

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(Received 23 August 1976)

In the past three years, a number of different interpretatons of the optical properties of LiF have appeared in the physics literature. We present new evidence which shows that most of these interpretations are incorrect in the soft-x-ray region, and for the first time we present measurements of anisotropies in the excitations in the ultraviolet region as a function of momentum transfer in single-crystal samples.

LiF is often thought of as the "hydrogen atom" of the insulators: It has the simplest atomic constituents and therefore its electronic properties ought to be understandable at a basic level. Nevertheless, in spite of a continuing effort over the years, including much recent activity,[1-8] there remain large gaps and discrepancies regarding its fundamental electronic excitations. In the present work, inelastic electron scattering spectra were obtained for LiF thin films using the Princeton inelastic scattering spectrometer.[9] Samples were of two kinds: polycrystalline thin films evaporated onto a thin Formvar substrate, and single-crystal self-supporting films prepared by mechanical polishing followed by ion milling. In each case the films were exposed to air for a short period of time after preparation and before measurement. Film thicknesses used in the results reported here varied from 1000 to 3500 Å. The data presented in this Letter have not been corrected for multiple scattering, although such an analysis has been carried out and will be presented at a later date. With the exception of experimental values of oscillator strengths, the present discussion depends only on the shapes of features and not on absolute values of the response function. Two kinds of new experimental results are presented here:

Localized excitations.—The operator which causes excitations in inelastic electron scattering is[10] $e^{i\vec{q}\cdot\vec{r}}$, where $\vec{r}$ is the position of an electron and $\vec{q}$ the transferred momentum. In the case of a localized initial state this operator may be expanded: $e^{i\vec{q}\cdot\vec{r}} = 1 + i\vec{q}\cdot\vec{r} + \frac{1}{2}(i\vec{q}\cdot\vec{r})^2 + \dots$. The first term does nothing since initial and final states are orthogonal; the second term, which causes dipole transitions, dominates for q sufficiently small; and the third term, which is a combination of monopole and quadrupole terms, becomes important for larger q. Thus when q is small, we observe the same excitations as are seen in optical adsorption studies, and at larger q, "forbidden" transitions may be observed.

Delocalized excitations.—If both initial and final states are extended in space (localized in momentum space) then the energy to create the excitation may vary with $\vec{q}$, allowing the dispersion of the excitation to be measured. For example, "direct" interband transitions may be excited between states at Γ in the valence band and states at X in the conduction band, again providing information not obtainable using optical absorption.

Figure 1 shows spectra measured at different momentum transfers in a single-crystal sample of LiF. For the moment, notice only the small feature near 35 eV which is present in the high-q curves but absent from those at low q. This feature appears at approximately the right energy to be a transition from the F 2s core state to the Li conduction band.[11] This transition should be optically forbidden at threshold and so, as explained above, should be absent in low-q data, and should increase in strength relative to the dipole transitions in proportion to q^2. To further verify identification, we have evaluated the oscillator strength for this transition using wave functions derived from the Herman-Skillman potentials.[12] The calculated and measured results are, respectively, $0.064q^2a^2$ and $(0.05 \pm 0.005)q^2a^2$, where a is the Bohr radius.

From x-ray-photoemission-spectroscopy (XPS) data,[3] the position of the F 2s level in LiF relative to the top of the valence band is 23.7 eV. Adding to this the recently redetermined optical band gap of 14.2 ± 0.3 eV,[7,8] we find an "inverse Koopmans' theorem" prediction of the transition energy of 37.9 eV. The major correction to this should be the exciton binding energy which is, then, 2.9 ± 0.3 eV. The binding energy of the F 2p transverse exciton has recently been determined to be 1.7 ± 0.3 eV.[7,8] This is the only case known to the authors in which binding energies of excitons associated with adjacent core levels has been determined. The striking increase in exciton binding energy with core binding energy is qualitatively consistent with a decrease in central cell corrections, but a quantitative understanding of these results is lacking at present.

Figure 2 shows spectra measured at $q = 0.34$ Å^{-1} and $q = 2.25$ Å^{-1} in the 52–67 eV range. The reason for choosing $q = 0.34$ Å^{-1} rather than $q = 0$ to compare with the high-q spectrum is so that both measurements are made under the same conditions, with the momentum transfer held at a finite value rather than being averaged over a range of values including zero. Including $q = 0$ brings in an energy-dependent factor which causes the entire spectrum to slope differently from $q \neq 0$. Multiple-scattering effects are negligible in the low-q spectrum, but are noticeable in the high-q re-

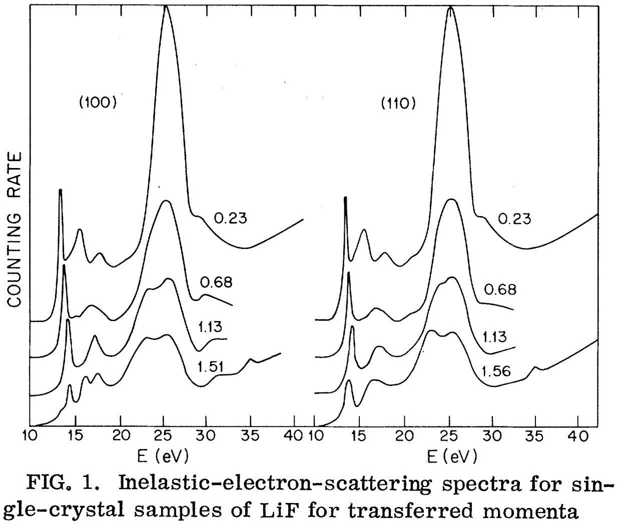

FIG. 1. Inelastic-electron-scattering spectra for single-crystal samples of LiF for transferred momenta along (100) and (110) directions in the Brillouin zone. Numbers near the curves indicate the magnitude of the momentum transfer in inverse angstroms.

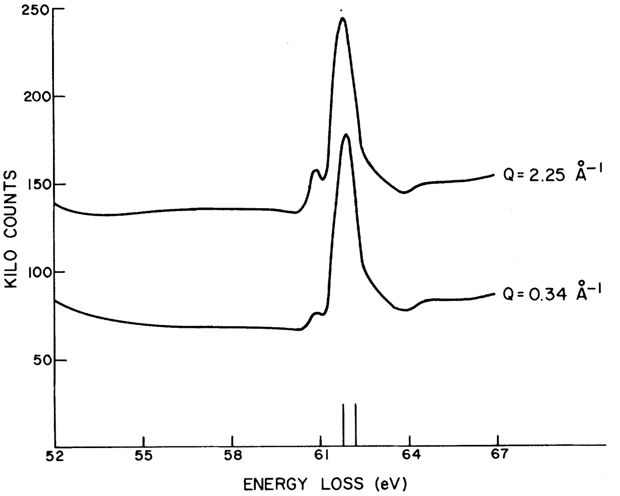

FIG. 2. Measurements using a polycrystalline sample in the soft–x-ray region for small and large momentum transfers. The vertical lines indicate the transition energies for the free-ion 1s–2s and 1s–2p singlet transitions.

sult. Such effects generally produce a sloping background, but can give rise to broad structure. For example, the ratio of the 62-eV peak height to the underlying background is different in the low- and high-q spectra, as is the overall slope in this region. These are typical multiple-scattering effects and cannot be regarded as significant.

This region of the spectrum has been the subject of much recent controversy. Two experimental papers,[3,5] describing results obtained using synchrotron radiation, reported observing weak structure beginning near 54 eV. Optical absorption studies yield information about the same transitions as low-q inelastic electron scattering, as explained above. We have accumulated a relatively large number of counts per point as shown in Fig. 2, yet there is no sign of such structure, either in the graph as shown, or in the raw digital data. We have repeated the low-q measurements on many samples with the same results, and have no explanation for this experimental discrepancy.

In addition, four theoretical papers[1,2,4,6] have concluded that forbidden optical transitions from the Li 1s shell should begin around 54 eV. It has been convincingly argued that the lowest energy transitions associated with a given core in an alkali halide are entirely excitonic.[6] What we expect then is an exciton associated with the Li 1s shell located near 54 eV which is weak and therefore difficult to observe using optical absorption because the transition is forbidden. From the above discussion it is clear why electron scattering is an ideal tool to test such a proposal. If optically forbidden transitions are occurring in this region then high-q spectra should make these transitions easily visible, as in the case of the F 2s exciton, even though the background is changing in magnitude and slope (see Fig. 1 near 35 eV).

In the entire range of 52–67 eV, the only peak which rises out of the background with an increase in q is the 61-eV feature, present also but more weakly in the low-q spectrum as a shoulder on the 62-eV peak. We are forced to conclude that this must be the only major forbidden excitation present in this energy range. This conclusion disagrees directly with previous experimental[3,5] and theoretical[1,2,4,6] results.

Because of this direct disagreement with previous work, we shall put this conclusion to a quantitative test. We hypothesize that the 61-eV peak is an atomic or excitonic Li 1s-2s forbidden transition. We should then be able to calculate the oscillator strength of the transition with reasonable accuracy using Herman-Skillman wave functions. The calculated and observed results are, respectively, $0.024q^2a^2$ and $0.011+(0.03 \pm 0.005)q^2a^2$. The major discrepancy between the two is the finite value in the low-q electron-scattering spectra. The peak is also visible in optical absorption measurements. The explanation of this discrepancy must be that the 1s-2s transition is only optically forbidden if the Li ion is at a position which possesses inversion symmetry, which is only true for a real Li ion in the absence of phonons.

Lattice vibrations have two major effects on the spectrum: They make forbidden transitions partially allowed, and they broaden spectral features. The rms even-parity value of the electron-lattice matrix element at room temperature is easily evaluated from the 62-eV linewidth to be 0.30 eV.[13] Odd-parity components of the electron lattice will mix the 2s and 2p states making the 1s-2s transition weakly allowed. From the strength of the low-q 61-eV peak the odd-parity rms value of the electron-lattice matrix element is evaluated to be 0.27 eV.[14] It is remarkable that these two values are essentially equal. For comparison, the rms value of the even-parity electron-lattice matrix element derived from the Gaussian width of the K edge in Li metal at room temperature is 0.126 eV.[15] Since an electron-phonon matrix element of reasonable magnitude can explain the observed intensity of the 1s-2s transition in the low-q spectrum, there appears to be no problem in identifying the 61-eV precursor of the 62-eV peak as the forbidden 1s-2s exciton.

Again using XPS data,[16] we find the binding energy of the 2s forbidden exciton to be 3.0 eV. The 2p allowed exciton is quite a different story. Band-structure calculations place the lowest p states in the conduction band approximately 6 eV above the conduction-band minimum. The 2p exciton therefore appears to have a binding energy nearly 3 times larger than that of the 2s exciton, even though one would expect these states to have roughly the same Coulomb interaction with the ion core. If this large binding energy were purely Coulombic, then we would expect the forbidden 2s exciton to be located near 54 eV, as has been proposed,[4,6] which Fig. 2 and the above discussion show not to be the case.

In the free atom or ion, the 2s and 2p states are nearly degenerate. In the solid, the 2p states

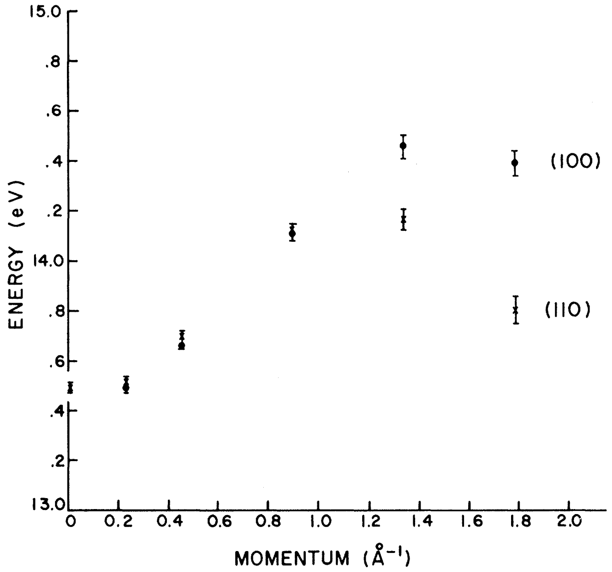

FIG. 3. Dispersion of the fundamental exciton in LiF. The zone boundaries in the (100) and (110) directions occur at 1.57 and 1.66 Å^{-1}, respectively.

lie approximately 6 eV higher than the $2s$ states. This upward shift is undoubtedly the result of overlap with the F ions which have large-radius $2p$ states to which the Li p states must be orthogonalized. The Li $2s$ states need only be orthogonalized to the F $2s$ and $1s$ states which are much smaller. So an extended $k=0$ Bloch state made up of Li $2p$ states feels a large repulsive overlap interaction with the F ions, while a localized $2p$ exciton does not. Thus, a 3-eV Coulomb interaction triggers an 8-eV repulsive interaction with the F ions to produce an effective 11-eV exciton binding energy.

It is clear from Fig. 1 that both the magnitude and direction of $\vec{q}$ affect the shape of the observed spectrum. One of the simplest results obtained from this data is the dispersion of the fundamental exciton. Figure 3 shows the measured peak position of the exciton as a function of $\vec{q}$ in both (100) and (110) directions. A completely localized exciton made up of a single Wannier function would show no dispersion, so the fact that we see any at all indicates that the exciton is somewhat delocalized. More quantitative conclusions require making some assumptions. Let us use an effective-mass approximation and assume that the exciton binding energy is constant throughout the Brillouin zone. Then it is easy to show that the small-q exciton dispersion is given by $E(q) = E(0) + [\hbar^2/2(m_e+m_h)]q^2$. The measured coefficient of q^2 is 1.0 eV Å^2. This gives $m_e+m_h = 3.8$. Most band-structure calculations for alkali halides result in $0.5 \leq m_e \leq 1$, and a corresponding reduced-mass range of $\mu^{-1} = 1.83 \pm 0.5$ The use of the measured exciton binding energy and $R = \hbar^2/2a_\mu^2$ yields $a = 2.0 \pm 0.25$ Å for the exciton radius. This corresponds to an rms momentum width of the $n=1$ exciton of $q = 0.5$ Å^{-1}. In this model, the fundamental exciton of LiF is not as localized as has been suggested,[2] and the $q=0$ peak is made from band states reasonably close to Γ, not spread throughout large regions of the zone.

Figure 1 contains a wealth of additional information which requires a serious calculation to be dealt with adequately. A few comments can be made, however. First, we see no hint of the splitting of the low-q plasma peak at 25 eV which has been previously reported.[17] At high q, especially near the the zone boundaries, we do see a partially resolved splitting of 2–3 eV. Whether this is a genuine splitting of the plasma collective mode due to the periodic field, as has been calculated for metals and semiconductors,[18] or whether it is an interband transition, is not known.

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*Work supported in part by the National Science Foundation under Grant No. DMR72-03168.

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Surface Resonances on the (100) Plane of Molybdenum

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(Received 20 September 1976)

Surface resonances on Mo(100) have been confirmed and studied in detail experimentally by field-emission energy distributions and theoretically by a linear-combination-of-atomic-orbitals calculation of the $\vec{k}_\parallel$-resolved surface local density of states. The experimental results in conjunction with the calculations have provided evidence of band-structure effects in field-emission energy distributions. The calculated results have also explained the angle-resolved photoemission results on W(100) and provided a clear picture as to the origin of these resonances.

The discovery[1] of an "anomalous structure" in the field-emission energy distributions (FEED) on W(100) and Mo(100) surfaces has stimulated intensive investigations into the origin and properties of this feature. Experimentally, this strongly surface-sensitive feature has been widely studied by FEED[2,3] and photoemission-energy-distributions (PED)[4-11] experiments. Theoretically, it has been attributed to a surface state with $\vec{k}_\parallel = 0$ ($\vec{k}_\parallel$ is the momentum parallel to the surface) located in the uppermost ("relative") d-band spin-orbit gap.[2,12] Later, it has been argued[13-15] that the observed peak was due to virtual surface states which exist in a large part of the surface Brillouin zone (SBZ), not just at $\vec{k}_\parallel = 0$. More recently, an argument based on nonrelativistic time-dependent relaxation effects[9] has been used to suggest that the origin of this surface state is the "absolute" d-band spin-orbit gap at lower initial-state energies.

In this Letter, I report the results of an experimental FEED study of the surface resonance peak on Mo(100) in conjunction with a theoretical calculation of the $\vec{k}_\parallel$-resolved surface local density of states (SLDS) on the same surface. I have found in FEED that the resonance peak on Mo(100) shifts to a lower energy and broadens in width as the step edge of the (100) plane is approached. In conjunction with the theoretical calculations, these phenomena confirm a known effect and a yet to be proved theoretical argument, namely, (1) the surface resonances on Mo(100) and W(100) possess a dispersive nature, and (2) the experimental field-emission current from the (100) faces of Mo and W is actually contributed to mostly, if not completely, by the states of finite $\vec{k}_\parallel$ in the SBZ as has been suggested theoretically.[13] In order to support this conclusion more strongly, I have made a numerical calculation of the $\vec{k}_\parallel$-resolved SLDS on Mo(100) based on a nonrelativistic nine-band (s, p, and d) tight-binding Green's function method.

The calculated results show that, just below the Fermi energy (E_F), there is a band of surface resonances which exist in a large part of the SBZ, primarily in the range of $|\vec{k}_\parallel| \lesssim 0.6\ \mathrm{\AA}^{-1}$. These resonances display dispersive characteristics. For example, in the vicinity of a major resonance ($k_x = 0.2884\ \mathrm{\AA}^{-1}, k_y = 0.0111\ \mathrm{\AA}^{-1}$) where the SLDS is extremely sharp and large at $\epsilon = -0.65$ eV, (a) the energy of the resonance decreases by 0.06 eV as k_y increases from 0.0111 to 0.122 $\mathrm{\AA}^{-1}$, and (b) the energy of the resonance increases by 0.4 eV as k_x increases from 0.15 to 0.45 $\mathrm{\AA}^{-1}$. The first result, (a), together with a necessary condition that the field-emission current is contributed mostly by the states of finite $\vec{k}_\parallel$ accounts for the observation in this FEED study. The second result, (b), together with the result that the SLDS of these resonances falls off dramatically as $|\vec{k}_\parallel| \gtrsim 0.6\ \mathrm{\AA}^{-1}$ accounts for the observations on W(100) by Willis, Feuerbacher, and Fitton.[9] Therefore this theo-