X-ray-absorption near-edge-structure studies in hexamethylenetetraselenafulvalene (HMTSF) and HMTSF-tetracyanoquinodimethane (HMTSF-TCNQ) and -tetrafluorotetracyanoquinodimethane (HMTSF-TFTCNQ)

P. M. Grant, W. D. Gill, and H. Morawitz

IBM Research Laboratory, San Jose, California 95193

K. Bechgaard

H. C. Ørsted Institute, Copenhagen, Denmark

D. E. Sayers

North Carolina State University, Raleigh, North Carolina 27650

We report the first x-ray-absorption measurements on conducting charge-transfer salts, using synchrotron radiation. By measuring the Se $K\alpha$ x-ray-absorption near-edge structure (XANES) of hexamethylenetetraselenafulvalene (HMTSF)^0 and fully charge-transferred HMTSF-tetrafluorotetracyanoquinodimethane (HMTSF-TFTCNQ) and comparing the results with those on partially charge-transferred HMTSF-tetracyanoquinodimethane (HMTSF-TCNQ), we conclude that the charge on the cation stack in the latter is delocalized as opposed to being concentrated on discrete sites of a generalized Wigner lattice.

One of the long-standing questions concerning the family of organic charge-transfer salts,[1] both insulating and conducting, has been the degree to which charge is localized or delocalized in the crystal lattice with respect to individual molecules. That is, does a given amount of charge spread out periodically along the quasi-one-dimensional cation and anion stacks, or does it segregate on isolated sites leaving some neutral and others fully ionized? On one hand, if electron (hole) charge is delocalized one might expect single-particle band-structure concepts to prevail, while on the other, localized electrons (holes) would exhibit strong correlation effects and otherwise display properties generally associated with Wigner-lattice models.

One might think that the two pictures would be readily manifest and separable by virtue of the difference in their transport properties, the former exhibiting metallic conductivity and the latter insulating or semiconducting behavior. However, as pointed out by Lieb and Wu[2] some time ago, a partially occupied Wigner lattice possesses, in principle, infinite mobility, at least in the Hubbard approximation. Since most of the conducting charge-transfer salts of interest have incomplete charge transfer, this picture is a plausible alternative to conventional band theory. To repeat, the question is whether this fractional charge becomes uniformly distributed or segregates onto a number of discrete sites leaving the remainder neutral. Torrance and Silverman[3] have dealt with the balance between partial charge transfer and ionic bonding, while Hubbard[4] has treated the question of optimum charge distribution among the sites of a partially occupied Wigner lattice possessing finite bandwidth.

Optical properties might also seem to provide a basis for distinguishing between the above two models. Metals should display reflectivity plasma edges, whereas localized systems usually have gaps appearing in their optical spectrum. Once more, the interpretation of the experimental evidence can become clouded. Strong charge-transfer transitions which exhaust their excitation-state manifold in a narrow energy range (e.g., an ideal Kramers doublet or a single exciton), give rise to reflectivity edges which are, by and large, difficult to distinguish from plasma edges. Alternatively, optical-phonon absorption on the low-energy side of a metallic plasma edge often gives the appearance of a gap in the itinerant-electron energy continuum.

Because the magnetic susceptibility in even the most highly conducting charge-transfer salts is markedly enhanced over its predicted Pauli value,[5] a high degree of correlation seems likely, yet even elemental metals show enhanced magnetic susceptibility[6]—it seems that there are almost no metals for which the classical Pauli model holds completely.

What then about core-level spectroscopy? It is well known that the amount of charge present in the valence orbitals of an ion affects the position of its core-energy levels, even down to the $1s$ shell. Core-level spectroscopy by x-ray photoemission (XPS), or electron spectroscopy by chemical analysis (ESCA), is universally used to determine atomic and molecular charge states in gases, liquids, and solids, and this tool has also been used on the problem under discussion by several groups with varying degrees of experimental success and unambiguous data interpretation. If the valence orbitals were localized, one would expect the emission peak corresponding to the core level in question to be shifted to some intermediate position between the energy observed for neutral species and that for full charge transfer. On the other hand, a discrete distri-

bution, creating an ensemble of neutrals and ions, should give rise to doublet absorption, each peak belonging to a respective ionic charge state.

The first attempts to address the localization versus delocalization question using core-level spectroscopy were the XPS studies by Grobman et al.[7] on the N $1s$ levels of TCNQ in (TTF)(TCNQ). They observed a doublet structure which they interpreted as a spectral superposition of neutral $TCNQ^0$ and fully charged $(TCNQ)^{-1}$ molecules. They proposed that the known value of charge transfer $(0.67e)$ arose from the relative amounts of these ions present as given by their respective absorption-peak intensity ratios. However, later XPS studies, made at normal and grazing electron-escape angles, by Swingle, Groff, and Monroe,[8] suggested that the doublet structure in N $1s$ observed by Grobman et al.[7] arose from a superposition of surface $(TCNQ)^0$ and bulk (TTF)(TCNQ) emission. A similar conclusion could be inferred from the ultraviolet-photoemission experiments of Schechtman, Lin, and Spicer[9] on (TTF)(TCNQ). The interpretation of Grobman et al.[7] was also challenged by Epstein et al.[10] who asserted that the observed doublet could be explained by different charge states on site-inequivalent nitrogen atoms on the same TCNQ molecule arising from a spatially varying Madelung potential. Grobman and Silverman[11] countered that intramolecular charge flow in response to the Madelung potential screened the difference in N $1s$ binding energies to levels below XPS experimental resolution, and there the matter seems to rest. Interpretive issues aside, it does seem clear that the sensitivity of photoemission measurements to surface conditions ultimately limits their usefulness with regard to the question of charge localization in bulk material.

A different approach to the problem of ascertaining molecular charge states was taken by Ritsko et al.[12] They used inelastic-electron-scattering spectroscopy (IES), a bulk absorption technique, to probe the chemical shift of N $1s$ in (TTF)(TCNQ). They found only one peak which, with the aid of semiempirical complete neglect of differential overlap (CNDO) calculations, they felt was more representative of $(TCNQ)^{-1}$ than $(TCNQ)^0$. Perhaps more significant was the fact they saw only a single peak, whereas a mixture of the negative and neutral ions as suggested by Grobman et al.[7] should have yielded a doublet split by 5 eV according to the former authors' calculations.[12] On the other hand, Ritsko et al.[12] did not calibrate their experiment by measuring known neutral and fully charged TCNQ compounds, thus leaving the door open so that their single observed peak was in fact actually a signature of delocalized partial charge transfer.

We decided to apply x-ray-absorption near-edge-structure (XANES) techniques to this problem for a variety of reasons,[13] not the least of which was that it had not yet been used on charge-transfer salts, and it was hoped that some new insights might be gained. Like inelastic electron scattering, it is a bulk- rather than surface-sensitive measurement. Unlike IES, sample preparation is easy and ultrahigh-vacuum conditions are not needed. Thus it is practical to study a variety of samples quickly without having to prepare extremely thin films. The principal experimental problem in XANES is

obtaining a sufficiently strong continuum source of x-ray radiation in the proper spectral region. As will be seen, this constraint precluded the study of members of the (TTF)(TCNQ) family because all of the elements present have $K\alpha$ edges which fall below the spectral range of the x-ray source available to us. Fortunately, there exists a series of selenium-containing charge-transfer salts which were ideal for our purposes. XANES also involves final-state processes. This could be construed as a complication vis-à-vis other photoemissive spectroscopies, but the fact is that XANES offers greater sensitivity than XPS to the valence condition of the atom undergoing excitation. Moreover, XANES does not produce an ionic final state whose charge could radically alter surrounding states— the so-called "localization" effect. Finally, XANES is particularly well suited to differentiate charge localization from delocalization. Within the "sudden approximation," the x-ray absorption occurs in about 10^{-18}–10^{-19} sec. This time is much shorter than the on-site residence period of a given carrier in a hopping-mediated transport process. We will discuss this point further below.

It may be helpful at this point to draw the reader's attention to a critical distinction that we have made based on different time scales. We assume the shortest time in the x-ray-absorption process to be the time for creation of the core-hole—equivalently the disappearance time of the x-ray photon—which we estimate by a golden-rule argument to be of order 10^{-18}–10^{-19} sec. In this part of the absorption process the initial state depends on the charge state of the ion or molecule in the surrounding lattice and, hence, the initial state will be able to differentiate between ionic and neutral lattices. On the other hand, the experimentally observed linewidth of several eV can be used to obtain an effective lifetime in the $(10^{-15}$–$10^{-17})$ sec regime. The remaining steps in the total absorption process depend on intraelectronic and interelectronic charge rearrangements (relaxation and screening) and core-hole lifetime effects (Auger and radiative decay) and are assumed to occur on a slower time scale. We do not have a detailed understanding of the various competing phenomena at this level, and our argument rests on the validity of the sudden approximation for the initial part of the absorption, which accounts for different charge states by shifts of the initial-state energy. We have lumped the slower (by several orders of magnitude) processes together as final-state effects and argue that the longest time scale in the problem is set by the core-hole lifetime which is an intra-atomic property of the Se moiety, not strongly dependent on the charge state of the molecule or molecular ion. Thus, the discussion that we give of the effects of finite bandwidth in the Wigner lattice which lead to a spectral broadening of the discrete neutral and ionic constituents, must be viewed from this perspective.

(HMTSF)(TCNQ) is a conducting charge-transfer salt showing quite high levels of metallic conductivity at room temperature.[14] For some time it was thought that the metallic state persisted to the millikelvin temperature range. It now seems clear that samples of high crystallinity undergo the usual periodic lattice distortion observed in most other compounds of this type.[15] Diffuse x-ray scattering indicates a partial charge transfer of $0.74e$ in

this material.[16] Recently, an isomorph, (HMTSF)-(TFTCNQF), has been synthesized which is insulating at all temperatures.[17] There is convincing evidence that this compound is fully charge transferred and is indeed a Mott-Hubbard insulator,[17] that is, its ionic state is completely $(HMTSF)^{+1}(TFTCNQ)^{-1}$. In addition, HMTSF itself exists as a neutral molecular crystal. Therefore, we had access to two compounds in which the amount of local cation charge was known [$(HMTSF)^0$ in crystalline HMTSF, $(HMTSF)^{+1}$ in (HMTSF)(TFTCNQ)] to use as standards to calibrate measurements on the local HMTSF charge state in (HMTSF)(TCNQ). Our experimental strategy was then as follows: (1) Measure the Se $K\alpha$ XANES in crystalline HMTSF (neutral and insulating) and in (HMTSF)(TFTCNQ) (insulating with one fully positive cation). (2) Measure the Se $K\alpha$ XANES in (HMTSF)(TCNQ) and observe whether the resulting spectra could be synthesized by a superposition of weighted spectra from the neutral and ionic standards. If total charge localization were present on the time scale of the absorption event, one would expect this scheme to work. A negative result would favor delocalization.

(HMTSF)(TCNQ) and (HMTFS)(TFTCNQ) were prepared by mixing boiling chlorobenzene solutions of the purified constituents. Following cooling, the precipitated crystals were filtered, washed with chlorobenzene, and vacuum-dried. Microanalysis (C, H, N) ensured 1:1 stoichiometry. The small needlelike crystals of each compound were milled into powder form using a mortar and pestle. The powder was then dispersed onto commercial adhesive tape for placement in the x-ray beam. Preliminary measurements were performed to determine optimum sample thickness to maximize the signal-to-noise ratio. The x-ray source was the SPEAR storage ring at the Stanford Synchrotron Radiation Laboratory operating at 3.1 GeV.[18] Polychromatic x ray emanating from the storage ring were dispersed by a double channel-cut silicon monochromator capable of 1.5 eV resolution in the energy range of interest ($\sim$12 keV). The monochromator

is separated from the storage-ring vacuum by a beryllium window which precluded experiments on elements lighter than chlorine. To our knowledge, we report here the first synchrotron-radiation measurements on conducting organic charge-transfer salts.

In order to demonstrate the sensitivity of the $K\alpha$ edge of selenium to its surroundings, we also measured the XANES of crystalline elemental Se and SeO_2. The results are shown in Fig. 1. Here the creation of an ionic state on selenium in SeO_2 results in a positive shift of about 4.7 eV for the principal absorption peak compared to neutral selenium. It is not clear whether this shift is due to movement of the Se $1s$ core level or the $4p$-derived final state, or both. The main absorption peak in both materials results from an exciton formed between the hole created in the Se $1s$ initial state and the electron excited to the final p-state manifold. The subsidiary structure at higher energies may arise from continuum resonances. The exact origin of much of the near-edge fine structure is unclear at this time. Its significance to us is that it most likely reflects changes in the molecular final-state environment due to differences in local charge density *before* absorption of the x ray by the selenium atom. We note that we consider energies up to 30 eV as belonging to the general $K\alpha$ near-edge region. Above this energy, we begin to see EXAFS arising from nearest-neighbor backscattering.

We next compare in Fig. 2 the edge structure of neutral Se to selenium in $HMTSF^0$. Now the principal peak shift is only about 2.5 eV, and, as in SeO_2, several subsidiary peaks appear above this peak. Again, we demur from interpreting the shift purely in terms of charge transfer. We only remark that Se in $(HMTSF)^0$ is expected to be slightly negative, thus leading to a core-level shift opposite in direction to that which would be seen in SeO_2.

Figure 3 contains the XANES spectra for $(HMTSF)^0$, (HMTSF)(TCNQ), and (HMTSF)(TFTCNQ). There are two principal observations to be made. The first is that there is very little shift in the position of the main exciton peak compared to that between elemental Se and SeO_2 and $(HMTSF)^0$. At most it is about 0.5 eV from $(HMTSF)^0$ to
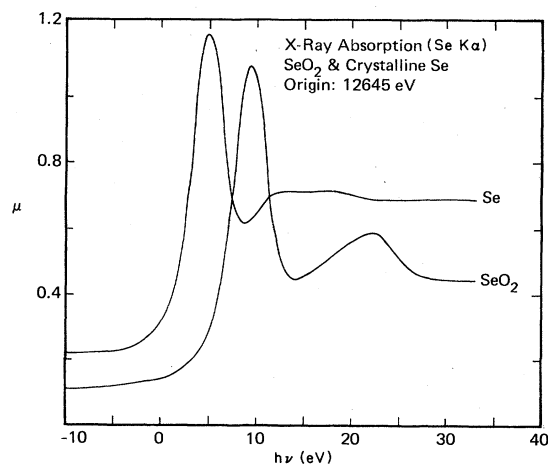

FIG. 1. X-ray absorption of the Se $K\alpha$ edge in crystalline elemental selenium and SeO_2. The absorption scale is in relative (dimensionless) units chosen to properly superpose the two spectra for graphical clarity.
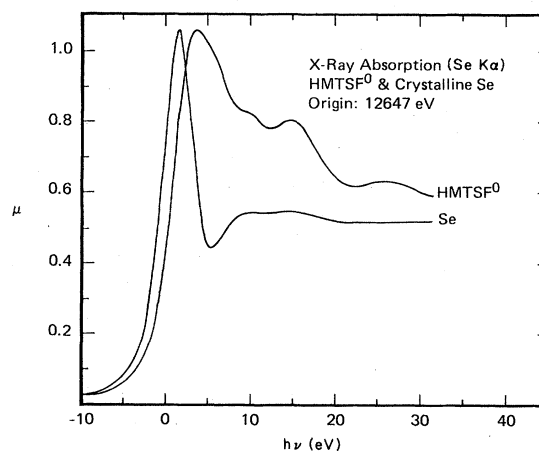

FIG. 2. Comparison of the Si $K\alpha$ edge in elemental Se and $(HMTSF)^0$. Absorption units are relative.

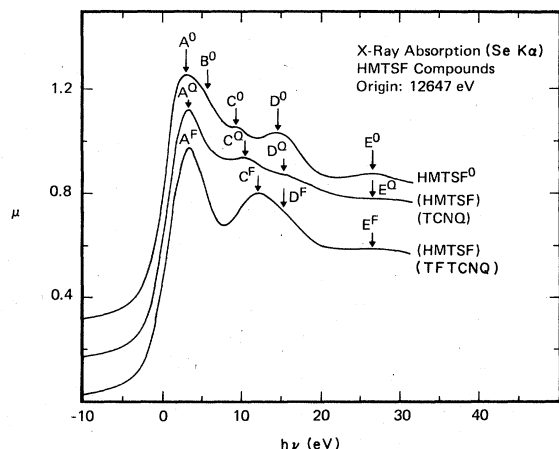FIG. 3. Se $K\alpha$ edges for $(HMTSF)^0$, $(HMTSF)(TCNQ)$, and $(HMTSF)(TFTCNQ)$. The noise level is roughly the width of the graphical trace. Reproducibility was better than 3% of the maximum signal strength. See the text for an explanation of the various spectral feature labels.

FIG. 4. Comparison of $(HMTSF)(TCNQ)$ with a synthesized spectrum containing weighted amounts of $(HMTSF)^0$ and $(HMTSF)(TFTCNQ)$ as shown.

$(HMTSF)(TFTCNQ)$. The single additional charge is distributed over the entire HMTSF molecule and not just on the seleniums. Perhaps 50% resides on the interfulvalene $C=C$ bond alone. Second, and more pertinent than the amounts of shift, is the fact that the total edge structure is qualitatively different for each of the three compounds. As shown in Fig. 3, we identify several spectral features as aids for discussion. We do not imply that a given peak labeled for one structure necessarily arises from the same source as a peak or shoulder labeled similarly on another. However, we did find that we could break down each spectrum using Lorentzian fitting procedures into one edge and five peaks that may have some possible intercompound relationship. Further interpretation will have to await the development of quantitative theories of XANES.[19] Focusing attention on $(HMTSF)^0$, we find besides the principal exciton at A^0, a shoulder B^0, two broad peaks C^0 and D^0, and a fifth broad hump E^0 which may be signaling the start of EXAFS scattering. In $(HMTSF)(TFTCNQ)$, shoulder B^F is missing and peaks C^F and D^F appear to be merged into a single broad feature. On the other hand, peaks C^Q and D^Q are separated in $(HMTSF)(TCNQ)$ as they are in $(HMTSF)^0$, yet no B^Q shoulder is present making it more like $(HMTSF)(TFTCNQ)$ in this respect. It is clear that it will be difficult to synthesize the $(HMTSF)(TCNQ)$ spectrum by superposing proportionally the neutral and cation spectra.

We have in fact tried to do just that in Fig. 4. Taking the Wigner-lattice model in its simplest aspect, namely, that exactly the right amount of neutrals and cations are mixed to give the measured charge transfer, we simply summed 74% of the normalized $(HMTSF)(TFTCNQ)$ spectrum to 26% of the normalized $(HMTSF)^0$ response. As Fig. 4 shows, it is apparent that we have failed to reproduce the experimental $(HMTSF)(TCNQ)$ spectrum. We therefore conclude that the generalized Wigner-lattice concept, in its most elementary form (zero-bandwidth lim-
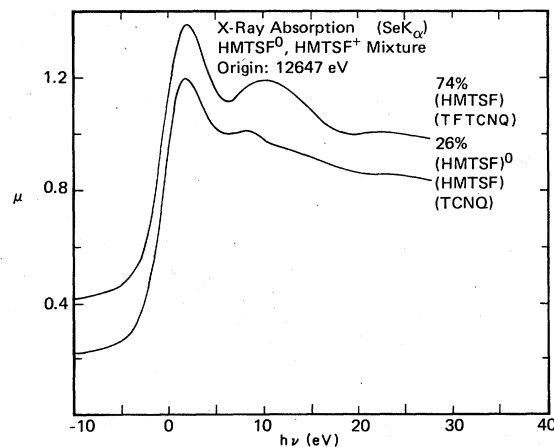
it), does not apply to $(HMTFS)(TCNQ)$.

Given this conclusion, the following question now arises: How does the introduction of finite bandwidth affect the optical properties of an incompletely occupied Wigner lattice? As Hubbard[4] has pointed out, the question of localization versus delocalization is ultimately one of relative time scales. To paraphrase his argument, a generalized Wigner lattice perturbed by a finite bandwidth can be thought of as switching between various charge configurations on a time scale of the order of the intermolecular transfer integral. Similar arguments have also been advanced by Nielsen, Epstein, and Sandman.[20] With use of 1 eV as a benchmark transfer integral energy,[21] the on-site residence time of a carrier in a perturbed Wigner lattice is of order 10^{-15} sec. As pointed out earlier, within the sudden approximation an x-ray-absorption event takes place on a scale of 10^{-19} sec for the Se $K\alpha$ edge.[22] Therefore, our measurements should have been capable of providing a "snapshot" of a discrete charge packet had one been present on a given site for the time indicated while hopping along the cation stack in $(HMTSF)(TCNQ)$. But what if the transfer integral were 10 eV? On the time scale of the x-ray absorption should not localization of the moving charge still be observed? The answer, of course, is that now the transfer integral is no longer just a perturbation on the correlation energy but is the dominant energy in itself. Therefore, the wave packet spreads, leaving a constant amount of fractional charge on each lattice site. We do not mean to imply that correlation and localization are not significant in other charge-transfer salts. The evidence is that correlation is at least as important as bandwidth in (TTF) $(TCNQ)$;[23] i.e., in the sense of the Hubbard model, $U \sim 4t$, where t is the transfer integral and U the on-site Coulomb correlation energy. In fact, these effects may be present on the TCNQ anion chain in $(HMTSF)(TCNQ)$ itself. However, we conclude that along the HMTSF stack, a bandwidth of the order ~ 1 eV is sufficient for charge spreading and for effective screening of potentials likely to enforce carrier localization.

As noted above, we believe this work to be the first application of XANES using synchrotron radiation to organic charge-transfer salts. In our opinion, this spectroscopic technique should find broad application to the type of problem addressed herein and promises to complement, and perhaps rival, more traditional spectroscopies, such as XPS, once better quantitative theories of the edge structure have been developed.[24,25]

ACKNOWLEDGMENTS

[1]In this paper, we use the following chemical symbols: HMTSF (hexamethylenetetraselenafulvalene, or 2,3,6,7-dipropano-1,4,5,8-tetraselenafulvalene), $(C_6H_6Se_2)_2$ with the structural formula 2,2'-bi(4,5,6-trihydro-1,3-diselenapentalene-2-ylidene); TCNQ (7,7,8,8-tetracyanoquinodimethane), $C_{12}H_4N_4$ or $H_4C_6[C(CN)_2]_2$ with the structural formula 2,2'-(2,5-cyclohexadiene-1,4-diylidene)bis(propanedinitrile-2-ylidene); TFTCNQ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane), $C_{12}F_4N_4$ or $F_4C_6[C(CN)_2]_2$ with the structural formula 2,2'-(2,3,5,6-tetrafluoro-2,5-cyclohexadiene-1,4-diylidene) bis (propanedinitrile-2-ylidene); TTF (1,4,5,8-tetrathiafulvalene), $C_6H_4S_4$ or $[(HCS)_2C]_2$ with the structural formula 2,2'-bi(1,3-dithiole-2-ylidene); TSF (1,4,5,8-tetraselenafulvalene), $C_6H_4Se_4$ or $[(HCSe)_2C]_2$ with the structure formula 2,2'-bi(1,3-diselenole-2-ylidene).

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