termined from the SHF spectra. The first excited state is observed at 94 cm^{-1} which agrees with the calculated position due to spin-orbit splitting reduced by a dynamic Jahn-Teller effect.

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Quasiatomic Auger Spectra in Narrow-Band Metals

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In this Letter it is shown that quasiatomiclike Auger spectra in narrow-band metals are a direct result of electron correlation effects. It is shown that if the "on-site" Coulomb interaction is much larger than the one-electron–band width, the Auger spectrum consists of an intense narrow atomiclike peak together with a weak broad bandlike peak at higher kinetic energy. On the other hand, if the Coulomb interaction is small the Auger spectrum will resemble the convolution of the band density of states convoluted with itself.

Some time ago it was proposed by Lander[1] that valence-band density-of-states information could be obtained from Auger spectra involving valence-band electrons. Using a one-electron–like picture and neglecting matrix-elements effects, Lander argued that the Auger line shape should be the valence-band density of states convoluted with itself. In numerous investigations, however, atomiclike Auger spectra have been found with hardly any visible band-structure effects. These atomiclike Auger spectra are common for narrow *d* bands whereas the spectra in which band-structure effects are found usually involve broad *s*-*p* bands. In recent investigations[2,3] of some 3*d*-series metals (Cu, Zn, Ga, Ge, As, and Se) it has been shown that all of the essential features of the $L_{23}M_{45}M_{45}$ Auger spectra can be explained in terms of an atomic model. The relative intensities of the final-state two-hole terms are in good agreement with atomic calculations, the term splittings are close to those calculated for the free atom, and even the satellite structure in Cu and Zn as well as the anomalous intensity ratio of the $L_2M_{45}M_{45}$ to the $L_3M_{45}M_{45}$ spectra are explained very well by use of an atomic model and a Coster-Kronig transition preceding the Auger transition.[4] The only substantial difference between the Auger spectrum in the metal and that in the free atom is a shift of the spectrum. This shift is due to extra atomic relaxation or polarization effects which effectively reduce the Coulomb interaction between the two holes in the final state. This polarization reduction of the two-hole Coulomb interaction is expected because of the highly polarizable medium in which the doubly ionized "atom" is situated.

This quasiatomiclike behavior is at first glance unexpected and has, to our knowledge, not been explained. Feibelmann, McGuire, and Pandey[5] have shown that matrix-element effects are important for the L_{23} VV Auger lines of Si. However this cannot explain the atomiclike spectra of the 3*d* and 4*d* metals because here the individual final-state terms are clearly seen with widths much less than the bandwidth.

In this Letter I give a simple physical picture based on well-known electron correlation effects and an exactly solvable model which describes the conditions under which quasiatomic Auger spectra in metals should be observed. With this theory one can, from the shape of the experimentally determined Auger spectrum, draw conclusions concerning the importance of electron correlation effects in the ground state of metals.

The model that I will use is based on the following considerations. The Auger transition rate is determined by matrix elements of the type

$$\int \Psi_c^*(r_1)\Psi_k^*(r_2)\,|r_1-r_2|^{-1}\Psi_{fi}(r_1)\Psi_{fj}(r_2)\,d\tau_1 d\tau_2. \tag{1}$$

Here Ψ_c is the wave function of the initial core hole, Ψ_k is that of the escaping Auger electron, and Ψ_{fi} is the wave function of the final-state hole in the band considered. I will use a Wannier representation so that in a tight-binding approximation Ψ_{fi} will be atomiclike orbitals and fi will label the site i and the quantum numbers L and S. The reason for using a Wannier representation will become obvious as we go on. Let the core hole be situated at the origin ($i=0$), in which case the largest contribution to the transition rate will be that where i and j in (1) are zero. This is the "intra-atomic" part. For i and $j \neq 0$, one gets the contribution from interatomic transitions which are expected to be about four to five orders of magnitude smaller,[6] so one may neglect them. This approximation is expected to be very good for tight-binding-like bands. For free-electron-like bands, the Wannier functions centered on sites other than the origin may still have a considerable amplitude at the origin and this approximation may no longer be valid.

I will also make the often-used sudden approximation, in which the interaction between the outgoing electron and the ionized material left behind is neglected as far as the shape of the Auger spectrum is concerned. In analogy to the photoelectron case[7] the spectrum will be given by the spectral distribution of the two-hole final state. To avoid cumbersome mathematics let us consider an S-like tight-binding band and neglect the finite lifetime of the core hole. The Auger-emission cross section will then be given by

$$d\rho/dE_k \propto \mathrm{Re}\,\pi^{-1}\int_0^\infty d\tau \langle d_{0\bar\sigma}{}^\dagger(\tau) d_{0\sigma}{}^\dagger(\tau) d_{0\sigma}(0) d_{0\bar\sigma}(0)\rangle \exp[i(E_c-E_k)\tau], \tag{2}$$

where d_σ creates a hole of spin σ at the site 0, E_c is the binding energy of the core hole, and E_k the kinetic energy of the outgoing Auger electron. The Fourier transform of the correlation function given in (2) can be written in terms of a Green's function such that

$$d\rho/dE_k \propto \mathrm{Im}\,G(\omega),$$

with $\omega = E_c - E_k$, and the Green's function has equations of motion given by[8]

$$\omega G(\omega) = (2\pi)^{-1}\langle [A,B]\rangle + \langle\langle [A,H];B\rangle\rangle_\omega, \tag{3}$$

where $A = d_{0\bar\sigma}{}^\dagger d_{0\sigma}{}^\dagger$ and $B = d_{0\sigma} d_{0\bar\sigma}$; and H is the Hamiltonian describing the electrons in the valence band.

A frequently used approximate Hamiltonian for describing tight-binding bands is the one introduced by Hubbard[9]:

$$H = \sum_{q\sigma}\eta_q d_{q\sigma}{}^\dagger d_{q\sigma} + U\sum_i n_{i\sigma} n_{i\bar\sigma}; \qquad n_{i\sigma} = d_{i\sigma}{}^\dagger d_{i\sigma}, \tag{4}$$

where U is the Coulomb interaction between two electrons on the same site and η_q is the one-electron–band dispersion relation. With this Hamiltonian the problem can be solved exactly for an initially filled band, since one is left with a two-particle problem.[10] The solution for large U(i.e., $U \gg 2W$, where W is the one-electron–band width) consists of $N(N-1)$ band states and N bound states lying outside of the band. To obtain the Auger line shape one can solve for $G(\omega)$ by the equation-of-motion technique as given in Ref. 3. We start with

$$G_{ml}{}^{00}(\omega) = \langle\langle \Psi_g | d_{m\bar\sigma}{}^\dagger d_{l\sigma}{}^\dagger ; d_{0\sigma} d_{0\bar\sigma} | \Psi_g\rangle\rangle_\omega, \tag{5}$$

where

$$d_{m\bar\sigma} = N^{-1/2}\sum_i \exp(-imR_i) d_{i\bar\sigma};$$

then

$$G(\omega) \equiv G_{00}{}^{00}(\omega) = N^{-1}\sum_{lm} G_{ml}{}^{00}(\omega),$$

and

$$[d_{m\bar\sigma}{}^\dagger d_{l\sigma}{}^\dagger, H] = -(\eta_l+\eta_m) d_{m\bar\sigma}{}^\dagger d_{l\sigma}{}^\dagger - \frac{U}{N}\sum_{kq} d_{m\bar\sigma}{}^\dagger d_{l+q,\sigma}{}^\dagger d_{k\bar\sigma}{}^\dagger d_{k+q,\bar\sigma} - \frac{U}{N}\sum_{kq} d_{k\sigma}{}^\dagger d_{k-q,\sigma} d_{m-q,\bar\sigma}{}^\dagger d_{l\sigma}{}^\dagger. \tag{6}$$

Because we are starting with a full band so that $d_{k\sigma}{}^\dagger\Psi_g = 0$, we move the annihilation operators to the left after which these terms will give zero contribution to the Green's function. The remaining terms are then

$$[d_{m\bar{\sigma}}{}^{\dagger} d_{l\sigma}{}^{\dagger}, H] = -(\eta_m + \eta_l + 2U) d_{m\bar{\sigma}}{}^{\dagger} d_{l\sigma}{}^{\dagger} + (U/N) \textstyle\sum_q d_{m-q,\bar{\sigma}}{}^{\dagger} d_{l+q,\sigma}{}^{\dagger}, \tag{7}$$

which result in

$$\omega G_{ml}{}^{00}(\omega) = (2\pi N)^{-1} - (\eta_l + \eta_m + 2U) G_{ml}{}^{00}(\omega) + (U/N) \textstyle\sum_q G_{m-q,l+q}{}^{00}(\omega). \tag{8}$$

We now go to an exciton notation so that

$$\begin{aligned} G_{KR}{}^{00}(\omega) &= N^{-1/2} \textstyle\sum_i \exp(-iKR_i) G_{i,i+R}{}^{00}(\omega) \\ &= N^{-1/2} \textstyle\sum_l \exp[i(K-l)R]\, G_{l,K-l}{}^{00}(\omega), \end{aligned}$$

then, since $G(\omega) \equiv G_{00}{}^{00}(\omega) = N^{-1/2} \sum_K G_{K0}$, we get

$$G(\omega) = \frac{1}{2\pi N} \sum_K \left(\frac{I(\omega, K)}{1 - UI(\omega, K)} \right), \tag{9}$$

where

$$I(\omega, K) = \textstyle\sum_l (\omega + \eta_{l+K/2} + \eta_{l-K/2} + 2U)^{-1}. \tag{10}$$

It should be noted here that since we are starting with a full band the average energy required to remove one electron will be $\langle \eta_l \rangle + U = E_d + U$. For U much larger than twice the bandwidth ($2W$) the Auger spectrum will consist of a strong, narrow atomiclike peak with a less intense broad-band–like spectrum appearing at higher kinetic energies. For $U \to 0$,

$$G(\omega) = (2\pi N^2)^{-1} \textstyle\sum_K \sum_l (\omega + \eta_{l+K/2} + \eta_{l-K/2})^{-1}, \tag{11}$$

the imaginary part of which is just the band density of states convoluted with itself as suggested by Lander.[1]

For large U ($U \gg 2W$) we can expand the Green's function around the pole corresponding to the bound state. Since the *one*-electron excitation spectrum is centered around $\langle \eta_l \rangle + U = E_d + U$, I define $\eta_l' = \eta_l - E_d$ and $\omega' = \omega + 2(E_d + U)$ and find

$$G(\omega') \approx \frac{1}{2\pi N} \sum_K \left[\omega' \left(1 - \frac{A^2(K)}{(\omega')^2} \right) - U \right]^{-1}, \tag{12}$$

where

$$A^2(K) = 4N^{-1} \textstyle\sum_l [(\eta_l')^2 + \eta_{l+K/2}' \eta_{l-K/2}'].$$

The poles will come at

$$\omega' \approx U + A^2(K)/U, \tag{13}$$

and the spectrum resulting from the bound states will then be given by

$$\operatorname{Im} G(\omega') \approx N^{-1} \sum_K \left(1 - \frac{A^2(K)}{U^2} \right) \delta\left(\omega' - U - \frac{A^2(K)}{U} \right). \tag{14}$$

In addition to this exciton or "quasiatomic" contribution to the spectrum, there will also be a wide spectrum corresponding to the poles appearing within the band. Since $A(k)$ is of the order of the one-electron–band width, we see that the total intensity in the atomiclike peaks will be approximately $1 - W^2/U^2$ and the width of the peak will be of the order of W^2/U. The rest of the intensity, i.e., W^2/U^2, will appear at higher kinetic energies in the region corresponding to the one-electron density of states convoluted with itself. The narrow bound-state spectrum will appear at a kinetic energy shifted down by approximately an amount U from that expected from 2 times a one-electron excitation. The one-electron excitation spectrum can be obtained from the photoelectron spectrum.

In a recent publication[3] U was determined from a combination of Auger and photoelectron spectra. The results for Cu, Zn, Ga, and Ge were discussed in detail and in all these materials it was found that $U > 2W$. It is therefore not unexpected in view of the theory presented here that the Auger spectra are atomiclike. In order to obtain an exact relation between the width and intensity of the atomiclike peaks and the one-electron band structure, one would have to work out the integrals appearing in (9). It is also interesting to observe that in the Auger spectrum of Cu there is a broad peak between the $L_3M_{45}M_{45}$ and $L_2M_{45}M_{45}$ regions of the spectrum. According to the present theory this would be due to the bandlike uncorrelated states.

The presented theory for Auger line shapes in metals has some very important consequences. This theory predicts that strong atomiclike peaks are expected in the Auger spectrum if electron correlation effects are important, whereas broad-band–like peaks are expected if the material is well described by a one-electron theory. Auger spectroscopy can therefore give insight into the importance of electron correlation effects. In order to compare theory in detail with experiments on d-band metals, the theory will have to be extended to degenerate bands and an approximate way of treating the partially filled bands will have to be developed.

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X-Ray Scattering Study of Spin-Lattice Dimerization in a Quasi One-Dimensional Heisenberg Antiferromagnet

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X-ray measurements on the quasi one-dimensional Heisenberg antiferromagnet TTF-(tetrathiafulvalenium-)$CuS_4C_4(CF_3)_4$ reveal a new crystallographic phase below $T_0 = 11$ K in which spin-$\frac{1}{2}$ TTF^+ units are paired. The temperature dependence of the order parameter below 11 K is accurately given by the BCS gap equation. Unexpectedly, the pairing is found along a diagonal direction in the $\vec{b}_F$-$\vec{c}_F$ plane rather than along the molecular stacking axis $\vec{c}_F$. Furthermore, strong diffuse scattering dominates the x-ray cross section at the dimerization superlattice positions for temperatures as high as 225 K.

The instability of one-dimensional (1D) antiferromagnetic systems to spin-lattice dimerization has been anticipated for over a decade.[1] Furthermore, the Hamiltonian used for a 1D antiferromagnetic system and that used to describe the Peierls instability in 1D conducting systems[2] are quite similar.[3] In spite of enormous effort, no quantitative synthesis of theory and experiment has yet been achieved for the 1D conductors. It is therefore of substantial importance to investigate the behavior of lattice-unstable 1D spin systems with a view toward understanding the general Peierls problem. In this Letter, we report on the results of x-ray diffuse scattering experiments in tetrathiafulvalene *bis-cis*-(1,2-perfluoromethylethylene-1,2-dithiolato)-copper [or TTF-CuBDT]. Using x-ray techniques we have (a) studied the structural nature of dimerization, (b) measured the order parameter, and (c) probed the dimensionality and spatial extent of the fluctuations. As we shall discuss below, each of these is of considerable importance in the