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Coulomb correlation in chromium compounds

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It is shown that the main features of chromium silicide photoemission spectra, unexplained by single-particle theory, can be understood quantitatively by the inclusion of Coulomb correlation effects. Our results provide the first direct evidence of the importance of correlation in metallic Cr compounds.

Although the electronic structure of transition-metal silicides has been the subject of intensive theoretical investigations,[1-7] several aspects of the experimental data have not yet been understood. One of the most intriguing points is to establish how much Coulomb correlation effects are important in determining the line shape of experimentally measured single- and two-particle spectra. Such effects are known to be significant in transition metals and are responsible for the occurrence of satellites and for the narrowing of the *d* bandwidth in the photoemission spectra.[8,9]

The aim of this Rapid Communication is to show that Coulomb correlation plays a very important role in the valence-band spectra of Cr silicides and that the inclusion of it in the theoretical calculations leads to a satisfactory description of the experimental data for these materials.

The inability of standard single-particle theory to explain the experimental energy distribution curves (EDC) is illustrated by Fig. 1, where the EDC's for $CrSi_2$ are compared with the outcomes of a density-of-states (DOS) calculation.[10,11] Since at this photon energy the photoemission cross section for Cr *d* orbitals is considerably larger than for *sp* orbitals, we give the Cr-derived 3*d* DOS only. The comparison shows that significant discrepancies exist both in the shape and in the location of the main structures. The experimental curve has a sharp maximum at 0.6 eV below E_F and a second broad spectral feature, centered around 1.7 eV. The theoretical curve shows peaks at −0.7, −1.8, and −2.4 eV, this last structure being the most intense feature of the DOS. The two main structures in the experimental spectrum have been associated with the nonbonding and bonding portions of the *d* band, respectively. Such an assignment is in agreement with the trend of the photoemission data for transition-metal disilicides[12] and is consistent with the current theoretical description of the chemical bond in silicides, according to which the coupling between Si *p* and metal *d* orbitals gives rise to bonding and antibonding states straddling the main *d* band.[1,2] The structures in the theoretical DOS have the same origin, but the *d* band appears broader than in the experimental curves; as a consequence the maximum in the bonding portion is located at higher binding energy. The relative intensity of these two maxima in the DOS is opposite of what is observed experimentally. The discrepancy cannot be simply imputed to final-state effects, since the features in the EDC's show little dispersion with photon energy and near the same intensity ratio for $h\nu$ ranging from 21 to 80 eV.[11] At higher photon energies the peak near E_F is attenuated by the presence of a significant modulation in the cross section due to the occurrence of a Cooper minimum (CM). As established by Rossi, Lindau, Braicovich, and Abbati[13] this modulation is smaller for the bonding states, so that near CM the second structure has a larger intensity. Therefore, if we consider experimental data far from CM, the shape of the EDC's should correspond to features in the occupied part of the DOS.

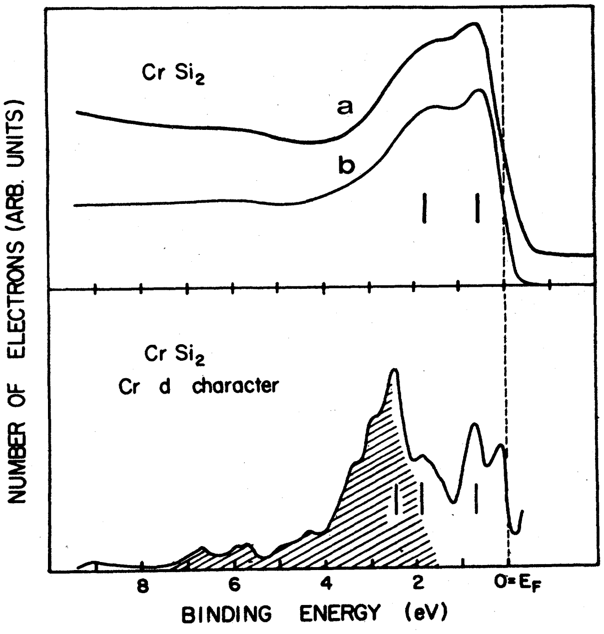

FIG. 1. Comparison of the valence-band emission of $CrSi_2$ with the theoretical *d*-partial DOS. Curve a EDC at $h\nu = 40$ eV; curve b EDC at $h\nu = 50$ eV.

The discrepancies cannot be imputed to inaccuracy in the calculated single-particle densities of state. The method used to obtain the theoretical curve of Fig. 1 has proved to be able to provide a description of the *d* states in agreement with more sophisticated band calculations for silicides of various transition metals (V, Ni, Pd).[3,5] For the case of Cr_3Si, for which a linear muffin-tin orbitals (LMTO) band calculation has also been performed,[14] we find that the shape of the *d*-band DOS is the same as in our calculations, while the differences in the binding energies of the main *d* peaks range between 0.2 and 0.4 eV. Such differences are considerably smaller than those found in comparing theory with experiment.

An aspect of the experimental curve in Fig. 1, which deserves a comment, is the presence of a weak structure around 6 eV. This structure is more clearly seen for $h\nu = 40$ eV and does not show a significant dispersion with the photon energy. Comparison with photoemission data for pure Cr indicates that it could be due to a *d*-band satellite.[15] In the case of pure Cr the satellite has a well-defined resonant behavior between 40 and 45 eV near the 3*p* excitation threshold.[15] To the authors' knowledge this narrow energy range has not yet been investigated in $CrSi_2$, so that an unambiguous assignment of the weak 6-eV structure cannot be done. However, its presence suggests that correlation effects play a significant role in the compound.

To check this conclusion and to see whether or not correlation effects can explain the difference between experimental and theoretical curves, we have performed a calculation of the single-particle spectrum of Cr silicides, including correlation. The theoretical approach we have used has been proposed by Treglia and co-workers[16] and has been successfully applied to the interpretation of single- and two-particle spectra of some pure transition metals[16,17] and of Ni silicides.[18] The basic idea of the method is to include the Coulomb correlation through a degenerate Hubbard Hamiltonian, which is solved perturbatively to second order in U/W (U is the Coulomb integral and W the bandwidth). In order to interpret the photoemission spectra it is assumed that the EDC's can be represented by the spectral function of the created hole

$$\tilde{n}(E) = -\frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{\infty} dE'\,\frac{n(E')}{E-\Sigma(E)-E'} ,$$

where $n(E)$ is the one-particle DOS and $\Sigma(E)$ is the self-energy. To second order in U the self-energy is given by

$$\Sigma(E) = 9U^2\int dE_1\int dE_2\int dE_3\{f(E_1)[1-f(E_2)][1-f(E_3)]+[1-f(E_1)]f(E_2)f(E_3)\}\frac{n(E_1)n(E_2)n(E_3)}{E+E_1-E_2-E_3} ,$$

where $f(E)$ is the Fermi factor.

Using these expressions we have calculated the single-particle spectra of Cr silicides. The densities of states were taken from our previous calculations.[11] The results for Cr_3Si, CrSi, and $CrSi_2$ are given in Fig. 2. Every part of the figure shows a comparison between the uncorrelated 3*d* DOS and the hole spectrum with correlation effects included. U was taken equal to 1.5 eV, which is the value that gives better agreement with the angle-resolved spectra of pure Cr.[17] To keep this term constant over the whole concentration range may seem at first sight a rather drastic approximation. Indeed we have found that changes of few tenths of eV in the U value should be considered in order to get the best agreement between the theoretical DOS and the experimental EDC's. However, these small changes are not very significant, in view of the accuracy of our single-particle calculations and of the simple perturbative approach used to include correlation effects. On the other hand, our purpose is not to fit the experimental data but to show that correlation is important in the description of the spectra.

The general features of the uncorrelated densities of state are similar in the three cases. In Cr_3Si and $CrSi_2$ one can distinguish four main structures. Two of them lie in the filled part of the DOS and, as already mentioned, are due to nonbonding and bonding *d* states, respectively. Antibonding states are responsible for the peaks at 2–4 eV above E_F, while the empty part of the nonbonding portion of the *d* band gives rise to the structures just above E_F. The splitting between the empty and filled part of the nonbonding *d* band depends upon the symmetry: it is more pronounced in Cr_3Si, whose DOS is reminiscent of the behavior of the *d* band in pure chromium. The splitting is absent in CrSi,

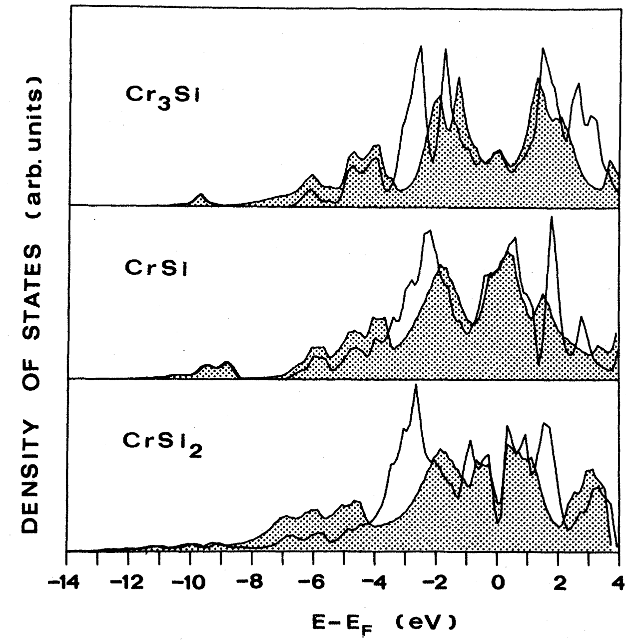

FIG. 2. Comparison between the Cr projected DOS computed with $U = 1.5$ eV (dotted areas) and the uncorrelated ($U = 0$) DOS.

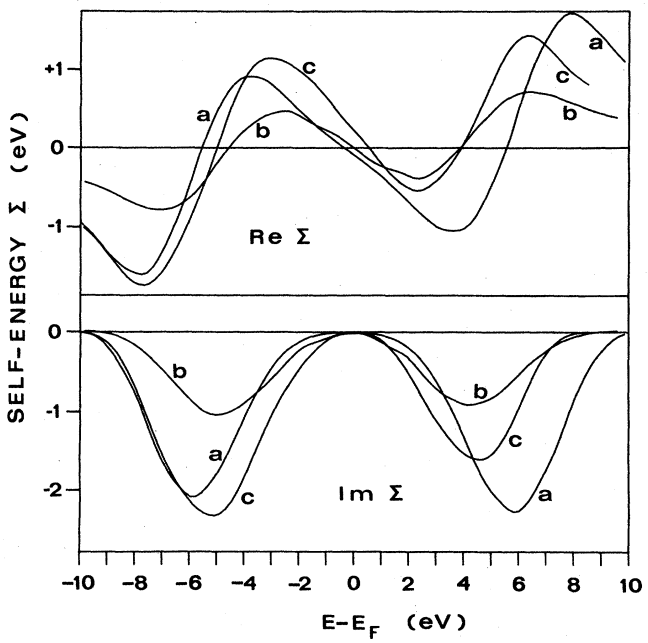

FIG. 3. Real and imaginary part of the self-energy for Cr_3Si (a), CrSi (b), and $CrSi_2$ (c).

where E_F falls at a maximum of the DOS, while it becomes a narrow notch in $CrSi_2$.

It is seen that the Coulomb correlation has dramatic effects on the electronic structure. All the peaks lying within 4 eV from the Fermi energy are shifted toward E_F. The displacement is more pronounced for the bonding and antibonding peaks than for the central part of the d band. As a consequence the band is more compact than in the uncorrelated DOS. The bonding structure undergoes a significant reduction in intensity. Part of its spectral weight is transferred to the satellite structure which develops around -6 eV. Similar changes take place in the upper part of the spectrum for the antibonding peak. The relative weight of the satellite structure compared with the intensity of the bonding peak is more pronounced in $CrSi_2$ than in Cr-rich compounds.

This behavior can be understood by considering the energy dependence of the self-energy. Figure 3 shows the curves of the real and imaginary part of the self-energy for these compounds. They represent essentially the shift ($\mathrm{Re}\Sigma$) and the broadening ($\mathrm{Im}\Sigma$) of the initial band states caused by the Coulomb correlation. It is clear from the figure that the reason why the central nonbonding portion of the d band is not significantly modified by the inclusion of the correlation is the fact that both quantities are small near E_F. The change in sign that takes place in the real part of Σ near E_F leads to the band narrowing. The large value of the imaginary part at lower energies determines the broadening of the satellite structure, while its position depends upon the location of the first minimum in the real part.

Turning to the comparison with the photoemission EDC, we notice that our results for $CrSi_2$ are in much better agreement with the experimental findings than the uncorrelated DOS. The intensity of the bonding peak is considerably smaller and the two main structures below E_F lie at 0.5 and 1.8 eV, respectively, very close to the observed values. Even the position of the satellite seems to correspond to the experimental observation, although at the present state of the investigation it cannot be identified very accurately in the EDC's. While this agreement confirms the importance of correlation, still the theoretical curve seems to overestimate the intensity of the bonding peak compared with the experimental data. We believe that such a detail can only be reproduced by a more accurate description of the photoemission process, where matrix element effects are taken into account.

In summary, we have shown that the understanding of experimental EDC's for Cr silicides can be achieved only by including correlation effects. It is likely that similar considerations apply to other transition-metal silicides and can be helpful in the interpretation of other spectroscopical data.

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