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Crystal-field and configuration dependence of hopping-matrix elements for $CeCu_2Si_2$

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The hopping-matrix elements $V_m(\varepsilon)$ between the conduction states with energy ε and the different crystal-field-split $4f$ states m are calculated for $CeCu_2Si_2$. With use of the Anderson impurity model, the effect of this m dependence on the static $T=0$ K susceptibility is studied. We also take into account that the one-particle hopping-matrix elements entering in the $f^0 \to f^1$ and $f^1 \to f^2$ hopping processes are different (configuration dependence). It is concluded that for $CeCu_2Si_2$ larger hopping-matrix elements are needed for the description of thermodynamic properties than for spectroscopic properties. These results are consistent with renormalization effects, which the Coulomb interaction between the $4f$ and conduction electrons is expected to cause.

I. INTRODUCTION

For many compounds with $3d$ or $4f$ electrons, the Hohenberg-Kohn-Sham density-functional formalism[1] gives an unsatisfactory description of important spectroscopic and thermodynamic properties, due to the strong correlation effects in these systems. In such cases it is customary to use a model Hamiltonian, e.g., the Anderson model,[2] to obtain a better description of the many-body effects. Recently, there has been much interest in obtaining the parameters of such a model from *ab initio* calculations using the density-functional formalism.[3]

In two previous papers[4,5] we have calculated the hopping-matrix elements $V(\varepsilon)$ for $CeCu_2Si_2$. While the calculated dependence on the energy ε for these hopping-matrix elements was essential in the description of the spectroscopic properties,[5] the overall magnitude was too large. Thus, it was found[4,5] that the square of the matrix element $V^2(\varepsilon)$ had to be reduced by a factor 0.45. It is interesting to examine whether this spectroscopic $V(\varepsilon)$ can also be used for describing thermodynamic properties, such as the susceptibility. The answer is not obvious, since the parameters in a model Hamiltonian are renormalized quantities and the renormalization may be different for different experiments. Recently, we performed calculations for a simple model containing the Coulomb interaction U_{fd} between a Ce $4f$ electron and the conduction electrons of the system.[6] These calculations suggested that, when a heavy-fermion system such as $CeCu_2Si_2$ is described in the Anderson model, larger values of $V(\varepsilon)$ should be used for thermodynamic properties than for spectroscopic properties. Preliminary calculations[4,5] actually suggested that one has to increase the spectroscopic $V^2(\varepsilon)$ by about a factor of 1.4 to describe the susceptibility. These calculations are, however, not conclusive, since they neglected that the hopping-matrix elements are different for the different crystal-field-split $4f$ levels. This difference should influence the thermodynamic properties, while spectroscopic properties should mainly sample the average of the different hopping-matrix elements. The purpose of this paper is to calculate this crystal-field dependence of the hopping-matrix elements and its influence on the susceptibility.

The hopping-matrix elements depend on the spatial extent of the Ce $4f$ wave function. This spatial extent depends on the occupation of the $4f$ level, since a larger occupation gives a less attractive potential and a more extended wave function. In a recent paper[7] we showed that to calculate the hopping from an f^n to an f^{n+1} configuration one should use the f^{n+1} configuration to generate the $4f$ wave function. For Ce this makes the square of the hopping-matrix element $V^2(\varepsilon)$ a factor of 2 larger for the f^1 to f^2 hopping than for the f^0 to f^1 hopping.[7] In addition, the matrix elements are strongly reduced in the presence of a core hole. It was argued[7] that in core-level x-ray photoemission spectroscopy (XPS) for Ce compounds, the effect of this strong configuration dependence on the relative weight of the two leading peaks is fairly weak because of a partial cancellation of opposing effects and that the use of the f^0 to f^1 hopping-matrix elements would be a reasonable approximation. It was further argued that for valence photoemission and for the static susceptibility it would also be reasonable to use the f^0 to f^1 hopping matrix elements, since the f^1 to f^2 hopping is less important for these properties. It would then be a reasonable approximation to neglect the configuration dependence when comparing two leading peaks in core-level XPS, valence photoemission, and the susceptibility. Here we want to check these arguments explicitly, and, in particular, we want to see if the consideration of the configuration dependence reduces the difference between the hopping-matrix elements needed for thermodynamic and spectroscopic properties.

We find that for $CeCu_2Si_2$ the inclusion of the dependence of $V_m(\varepsilon)$ on the crystal-field-split levels m has a moderate effect on the susceptibility. In agreement with earlier calculations, we therefore find that a larger $V(\varepsilon)$ is needed for the description of the susceptibility than for the spectroscopic properties. This is consistent with the expected effects of the Coulomb interaction U_{fd} between the Ce 4*f* electrons and the conduction electrons. For $CeCu_2Si_2$ and for the studied properties, the effects of the configuration dependence are not very drastic, as expected. In Sec. II we calculate the hopping-matrix elements, in Sec. III we study the susceptibility, and in Sec. IV the spectroscopic properties. The results are summarized in Sec. V.

II. CALCULATION OF HOPPING-MATRIX ELEMENTS

We use the Anderson impurity model[2] which includes the extended (conduction) states of the system as well as the 4*f* electrons at one site. The Hamiltonian is written as

$$H=\sum_m \left[\int d\varepsilon\, \psi^\dagger_{\varepsilon m}\psi_{\varepsilon m} + \varepsilon_m n_m + \int d\varepsilon [V_m(\varepsilon)\psi^\dagger_m \psi_{\varepsilon m} + \text{H.c.}] \right] + U \sum_{m<m'} n_m n_{m'} \, . \tag{1}$$

The localized 4*f* states are labeled by a quantum number m and have the energy ε_m. It is assumed that the conduction states can be transformed in such a way that each state couples strongly to at most one 4*f* state m, and that the coupling to other states m' can be neglected.[8] Such a state is then labeled by m and the energy ε. Extended states which do not couple to any 4*f* state are not included in the Hamiltonian. The first two terms describe the energies of the extended and localized states, respectively, and the third term describes the hopping between these two sets of levels. The fourth term describes the Coulomb interaction between the 4*f* electrons. The hopping-matrix elements can be obtained from the projected 4*f* density of states $\rho_m(\varepsilon)$ in a density-functional calculation:[9]

$$V_m^2(\varepsilon) = -\frac{1}{\pi}\text{Im}\left[\int d\varepsilon' \frac{\rho_m(\varepsilon')}{\varepsilon-\varepsilon'-i0^+} \right]^{-1} \, . \tag{2}$$

We have performed density-functional calculations for $CeCu_2Si_2$ using the local density approximation (LDA).[1] These calculations give a 4*f* occupation of about 1.38. To obtain hopping-matrix elements appropriate for f^0 to f^1 hopping, the 4*f* wave function should, however, be calculated for the occupation one.[7] To take this into account, we have rescaled the calculated hopping-matrix elements by a factor $\sqrt{0.77}$ $[V^2(\varepsilon)\rightarrow 0.77V^2(\varepsilon)]$. We have used the crystal-field-level scheme of Horn *et al.*[10] In this scheme the levels are given by

$$\begin{aligned} |0\rangle &= a|\pm\tfrac{5}{2}\rangle + b|\mp\tfrac{3}{2}\rangle \, , \\ |1\rangle &= |\pm\tfrac{1}{2}\rangle \, , \\ |2\rangle &= b|\pm\tfrac{5}{2}\rangle - a|\mp\tfrac{3}{2}\rangle \, . \end{aligned} \tag{3}$$

Here $|m\rangle$ on the right-hand side refers to a state with the quantum numbers $j=\frac{5}{2}$ and $m_j = m$. Horn *et al.*[10] gave the coefficients $a=0.83$ and $b=0.56$. The results are shown in Fig. 1. A Lorentzian broadening of 0.13 eV (full width at half maximum) has been introduced by using a finite (0.065 eV) imaginary part in the denominator of Eq. (2). The different states couple in a rather different way to the conduction states. State $|1\rangle$ has a weak coupling to the states at the Fermi energy ($\varepsilon=0$), while the state $|0\rangle$ has a relatively strong coupling. The coupling to the states at -8 and at -9 eV, for instance, is also very different for $|0\rangle$ and for $|1\rangle$.

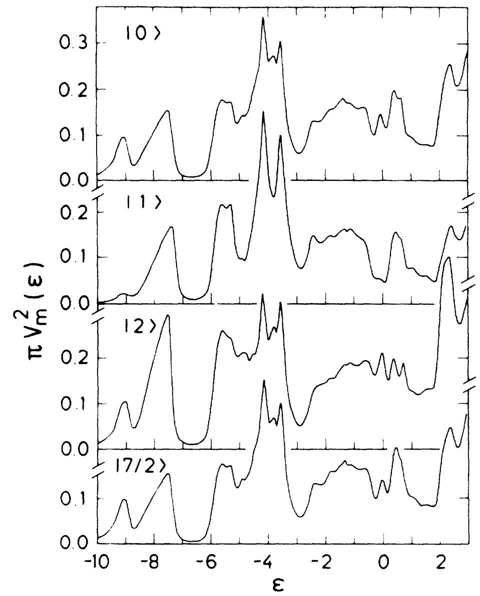

FIG. 1. Hopping-matrix elements $V_m^2(\varepsilon)$ for $CeCu_2Si_2$. The labels $|0\rangle$, $|1\rangle$, and $|2\rangle$ refer to the levels in the crystal-field scheme of Horn *et al.* (Ref. 10) for the $j=\frac{5}{2}$ level, and $|\frac{7}{2}\rangle$ to an average over all the $j=\frac{7}{2}$ levels. The energy zero is at the Fermi energy and all energies are in eV.

III. SUSCEPTIBILITY

We have calculated the static $T=0$ susceptibility χ using a method developed earlier.[11] This method is based on a variational approach which treats the inverse degeneracy of the 4*f* level as a small parameter. We introduce a basis state in which the conduction states $|\varepsilon m\sigma\rangle$ are filled up to the Fermi energy and in which the 4*f* levels are empty (0 in Fig. 2). This basis state couples to basis

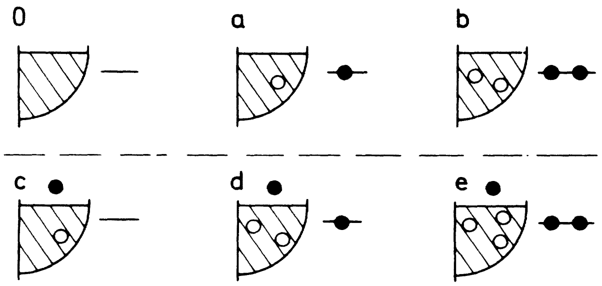

FIG. 2. Schematic description of basis states. The solid circles on the horizontal line represent 4*f* electrons, the open circles represent conduction holes, and the solid circles represent conduction electrons.

states with one $4f$ electron and a conduction hole ("a" in Fig. 2). These new basis states couples to basis states with two $4f$ electrons and two conduction holes ("b" in Fig. 2). States with more than two $4f$ electrons are neglected because of the large Coulomb interaction for such states. These three sets of basis states (first row in Fig. 2), give the correct ground state to lowest order in the inverse degeneracy. We refer to this as a first-order calculation. We further add basis states with one conduction electron and one conduction hole ("c" in Fig. 2) which couple to the states with one $4f$ electron and one conduction hole. These states give the most important contributions to next order in the inverse degeneracy. We refer to this as a second-order calculation, although we have neglected other states ("d" and "e" in Fig. 2) of the same order in the inverse degeneracy. Within this basis set we perform a variational calculation and obtain the ground state $|\phi\rangle$. The susceptibility is then calculated from the equation[11]

$$\chi=2\langle\phi|S_z(H-E_0)^{-1}S_z|\phi\rangle \ , \qquad (4)$$

where H is the Hamiltonian, E_0 is the ground-state energy, and S_z is an operator which describes the coupling to an external magnetic field. The evaluation of Eq. (4) is performed by inserting intermediate states on both sides of $(H-E_0)^{-1}$. The matrix elements of $(H-E_0)$ are then calculated and the corresponding matrix is inverted.[11] Here we have chosen the operator S_z so that it corresponds to the $q=0$ susceptibility parallel to the c axis.

The intermediate states used to evaluate Eq. (4) form a basis set for the final states reached in inelastic neutron scattering. They are of the same type as the ones in Fig. 2, except that there is no state of the type 0. The label m is a good quantum number. We can then diagonalize the Hamiltonian in the space of intermediate basis states corresponding to a given value of m, and obtain the lowest energy E_m in that space. The differences between the E_m's determine the crystal-field splittings. These differences are not the same as the differences between the ε_m's, since the former contain effects of the hopping-matrix elements. The energy of the $4f$ level is written as $\varepsilon_m \equiv \varepsilon_f+\Delta_m$, where $\Delta_0=0$. The parameter $\varepsilon_f=-2.4$ eV is obtained from the spectroscopic experiments,[5] and the values of Δ_m are adjusted so that the experimentally observed[10] crystal-field splittings (E_m) are obtained. We have also used the value of U deduced from the spectroscopic experiments.[5]

We now calculate the susceptibility using the hopping-matrix elements $cV_m(\varepsilon)$. The value of the empirical parameter c is adjusted so that the experimental[12] value ($\chi \sim 2.5\times10^{-2}$ emu/mole) is reproduced, and c is therefore a measure of how much the magnitude of $V_m(\varepsilon)$ is overestimated by the calculations. The results are summarized in Table I. We first perform a first-order calculation using the hopping-matrix elements appropriate for f^0 to f^1 hopping. We find that to obtain the experimental susceptibility we have to use the prefactor $c^2=0.72$ of the hopping-matrix elements. This is to be compared with the spectroscopic value $c^2=0.45$. To check the convergence in terms of the size of the basis set, we have performed a second-order calculation. This increases the susceptibility by about a factor 1.5. However, the susceptibility depends on the hopping-matrix elements in an exponential way. It is therefore sufficient to increase c^2 by just 1% to recover the experimental susceptibility. We also find that replacing the proper matrix elements $V_m(\varepsilon)$ by an average over all values of m has a moderate effect on c^2 for $CeCu_2Si_2$. Thus, it is sufficient to change c^2 to about 0.67 to obtain the experimental χ. To check the importance of including the basis states with double occupancy of the $4f$ level [state "b" in Fig. 2] we have put $U=\infty$. We then find that χ is increased by an order of magnitude. This increase is not quite as dramatic as in the first-order calculation.[5] In the second-order calculation an increase of c^2 to 0.80 leads to the experimental χ for $U=\infty$. Finally, we have considered the configuration dependence in a calculation with a finite U. This leads to a rather large reduction of χ, and we now must reduce c^2 to 0.63 to obtain the experimental χ.

IV. SPECTROSCOPIC PROPERTIES

In this section we discuss the valence ($4f$) and core-level ($3d$) photoemission spectroscopies (PES). In Fig. 3 we show results for the $4f$ PES spectrum and in Fig. 4 results for the $3d$ PES core spectrum. The method for calculating these spectra has been described earlier.[8] All multiplet effects are neglected, which may have an appreciable effect on the core spectrum, where the f^2 configuration plays a substantial role. For the core spectrum we have introduced a Gaussian broadening of 1.2 eV full width at half maximum (FWHM) to simulate the instrumental resolution and a Lorentzian broadening of 1.4 eV (FWHM) to describe the lifetime effect. For the valence spectrum, the instrumental resolution is simulated by a Gaussian broadening of 0.6 eV (FWHM). As earlier,[13] we also introduce a Lorentzian broadening of 0.6 eV (FWHM) to simulate other broadening effects, for instance, dispersion due to lattice effects. Figures 3(a) and 4(a) show the results obtained by adjusting the $4f$ level position ε_f and the parameter c^2 to obtain the optimum agreement with experiment, as discussed earlier.[5] This leads to $\varepsilon_f=-2.4$ eV, as also used in the susceptibility calculations, and to the value $c^2=0.45$ quoted in Table I. We can see that one set of parameters gives a rather satisfactory description of the experimental spectra. In particular, we note that, to obtain a proper description of the

TABLE I. Values of the empirical factor c^2 in $c^2V^2(\varepsilon)$ for different calculations.

	Spectroscopic	Susceptibility				
		First order	Second order	Average $V^2(\varepsilon)$	$U=\infty$	Configuration dependence
c^2	0.45	0.72	0.73	0.67	0.80	0.63

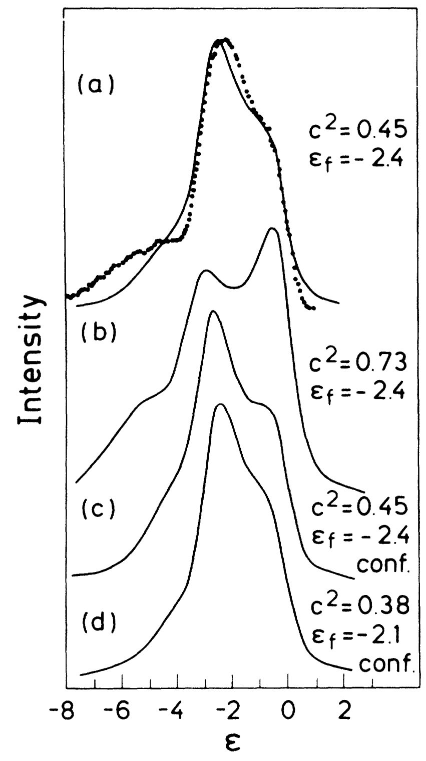

FIG. 3. The $4f$ valence spectrum. In (a) we show results for $c^2=0.45$ and $\varepsilon_f=-2.4$ eV, in (b) c^2 has been increased to 0.73, in (c) the configuration dependence is taken into account for $c^2=0.45$, and in (d) we use $c^2=0.38$, $\varepsilon_f=-2.1$ eV including the configuration dependence. The experimental results are from Kang *et al.* (Ref. 5). All energies are in eV.

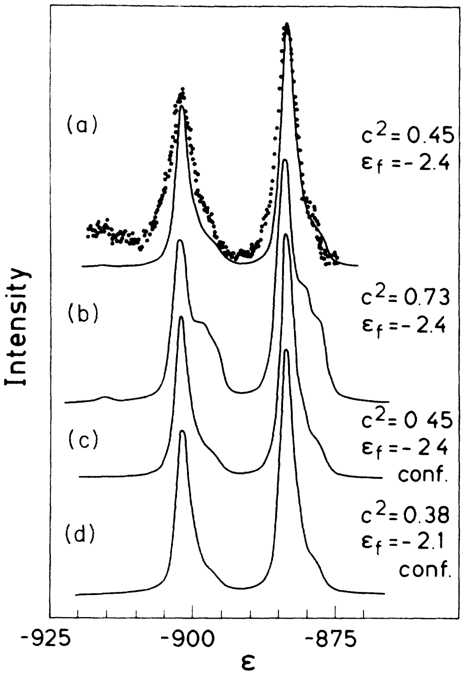

FIG. 4. The $3d$ core-level spectrum. The meaning of (a)–(d) is the same as in Fig. 3. The experimental results are from Kang *et al.* (Ref. 5). All energies are in eV.

valence spectrum, the energy dependence of $V(\varepsilon)^2$ is essential.[5] In the core spectrum the two shoulders at about -878 and -897 eV are particularly sensitive to the magnitude of the hopping-matrix elements. These shoulders correspond to final states of mainly f^2 character. In the valence spectrum the shoulder at the Fermi energy ($\varepsilon_F=0$) and the width of the spectrum are sensitive to the hopping-matrix elements.

In Figs. 3(b) and 4(b) we have increased the value of c^2 to 0.73, the value needed to obtain the experimental static susceptibility. This value is much too large for both spectroscopies. In the $4f$ spectrum there is now too much weight at the Fermi energy and the width of the spectrum is also too large. In the core spectrum the f^2 peaks have too much weight. We can clearly say that $c^2=0.73$ is much too large for describing the $4f$ and $3d$ spectra.

Figures 3(c) and 4(c) were obtained by including the configuration dependence. As suggested earlier,[7] the effect is moderate for Ce compounds, although we do not expect this to be true in general. The valence spectra in the third row has a somewhat too pronounced peak at the Fermi energy, although the weight of this peak is approximately correct. The shape of the peak can be modified by reducing c^2 further to 0.38, if at the same time the $4f$ level is raised to -2.1 eV. This is shown in Figs. 3(d) and 4(d). Using the value $\varepsilon_f=-2.1$ eV and including the configuration dependence, we find that $c^2=0.59$ is needed to obtain the experimental susceptibility. The inclusion of the configuration dependence may therefore reduce the discrepancy between the thermodynamic and the spectroscopic value of c^2 somewhat, but the accuracy in the approach is not sufficient to establish this.

V. CONCLUDING REMARKS

We have calculated the hopping-matrix elements $V_m(\varepsilon)^2$ for the different crystal-field-split $4f$ orbitals using the crystal-field scheme of Horn *et al.*[10] As can be seen in Fig. 1, there is a substantial variation between the different levels. We nevertheless find that, for $CeCu_2Si_2$, the effect on the susceptibility is not very drastic, as is illustrated by the change of c^2 in Table I when we use a $V(\varepsilon)^2$ averaged over the crystal-field-split levels. In general, the effect may be much larger. We have illustrated that the magnitude of $V(\varepsilon)^2$ needed to describe a thermodynamic property, such as the susceptibility, is larger than what is needed to describe the spectroscopic properties. Some of this discrepancy may be removed when the configuration dependence of the hopping-matrix elements is taken into account. As expected, for Ce compounds the configuration dependence has, however, not very drastic effects on the static susceptibility and the spectroscopic properties studied here. Our results therefore are consistent with our earlier conclusion[6] that, for heavy-fermion systems, the renormalization of the hopping-matrix elements by the Coulomb interaction between the $4f$ electrons and the conduction electrons leads to larger hopping-matrix elements for thermodynamic properties than for spectroscopic properties.

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