

## Electronic structure of chromium and manganese impurities in copper

D. Bagayoko,\* P. Blaha,<sup>†</sup> and J. Callaway

*Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803-4001*

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We have performed self-consistent calculations of the electronic structures of chromium and manganese impurities in an fcc copper matrix. The calculations employed a linear combination of Gaussian orbitals procedure applied to the 19-atom clusters  $\text{CrCu}_{12}\text{Cu}_6$  and  $\text{MnCu}_{12}\text{Cu}_6$ . No shape approximation was made to the potential which was chosen according to the local-spin-density functional approximation. We discuss the electronic levels and the related cluster density of states and the charge and spin densities. The Fermi level lies on a partially occupied  $t_{2g}$  up-spin state in the case of the Cr impurity. A total cluster moment of  $4.00\mu_B$  with  $3.53\mu_B$  localized at the chromium site was obtained. In the case of the manganese impurity the Fermi level coincides with a down-spin  $a_{1g}$  state with up-spin  $a_{1g}$  and  $t_{2g}$  states, quasidegenerate, just below it. The total and local moments are, respectively,  $5.00\mu_B$  and  $4.04\mu_B$ . The spin density is negative at the nuclear sites for both impurities and the first-shell copper atoms. We provide some details of the good agreement with experiment. The comparison with previous calculations yields mixed results.

### I. INTRODUCTION

Progress in the study of dilute alloys is concurrently sustained by well-established experimental techniques and improving computational schemes capable of probing of electronic, magnetic, and transport properties of these systems. Some basic principles involved in the various experiments have been described elsewhere.<sup>1,2</sup> We have, among the experimental methods used to investigate the properties of Cu-Cr alloys, transmission conduction-electron spin resonance,<sup>3</sup> de Haas-van Alphen,<sup>4</sup> and nuclear magnetic resonance (NMR) studies,<sup>5-7</sup> as well as susceptibility measurements.<sup>8,8</sup> Similar results are available<sup>4-8</sup> for copper-based manganese alloys, Cu-Mn, along with other systems.

Kondo<sup>10</sup> and other authors,<sup>11-13</sup> have discussed theoretical models of dilute magnetic alloys. In a fundamental paper<sup>13</sup> Anderson presented a simple theory of moment formation which has provided the basis for many further developments. Studies specifically related to our investigations include the NMR model calculations of Cohen and Slichter<sup>14,15</sup> who interpreted some Knight-shift data pertaining to Cu-Cr, Cu-Mn, and other alloys. Johnson *et al.*<sup>16</sup> presented  $X\alpha$  scattering wave calculations of the electronic structure of the finite system  $\text{MnCu}_{12}\text{Cu}_6$ , i.e.,  $\text{Cu}_{16}\text{Mn}$ . Their work encompassed several other clusters,  $M\text{Cu}_{12}\text{Cu}_6$ , where  $M$  is V, Fe, Ni, or Cu. Instead of a cluster approach, as used by Johnson *et al.*, several other calculations<sup>17-19</sup> employed the Green's function Korringa-Kohn-Rostoker (KKR) method. These calculations determined the electronic structures of substitutional  $3d$  impurities in an otherwise perfect fcc copper crystal. The KKR calculations disagreed with the results of Johnson and co-workers. Podloucky *et al.*<sup>16</sup> concluded from these discrepancies that the cluster approach is inadequate for the description of these systems. However, other recent cluster-approach calculations based on local spin-density functional poten-

tials in a linear combination of Gaussian orbitals (LCO's) procedure appear to be more satisfactory. Lee *et al.*<sup>20-22</sup> obtained results in good agreement with experiment for pure clusters of nickel and iron. Blaha and Callaway<sup>23</sup> studied Fe, Co, and Ni impurities in one- and two-shell fcc copper matrices. These authors obtained good agreement with experiment as well as with some KKR results.

This work is concerned with chromium and manganese impurities in copper; the electronic structures and related quantities for  $\text{Cu}_{18}\text{Cr}$  and  $\text{Cu}_{18}\text{Mn}$  are presented. The method employed in these self-consistent calculations, the same as that used by Blaha and Callaway,<sup>23</sup> is briefly described in Sec. II. This is followed by a detailed presentation of our results for  $\text{Cu}_{18}\text{Cr}$  and  $\text{Cu}_{18}\text{Mn}$  in that order. These results are compared to previous experimental and theoretical findings. Section IV, the conclusion, includes some notes on general trends for  $3d$  impurities in fcc copper.

### II. METHOD

Our self-consistent calculations employed the cluster approach. We considered free clusters only. This implies that interactions which extend beyond the second shell are ignored. The clusters considered are all face-centered cubic, with a lattice constant of 6.83 a.u. We utilized the local-spin-density functional potential of Rajagopal, Singhal, and Kimball (RSK).<sup>24</sup> The single-particle functions are expanded as symmetrized linear combinations of Gaussian orbitals; the orbitals employed are those determined for free atoms by Wachters.<sup>25</sup> No contraction of the basis set was made; we used 14  $s$ -, 9  $p$ -, and 5  $d$ -type functions centered on each atomic site. The basis sets for the first- and second-shell atomic sites were those for the copper atom, while the basis for the central site was that for the impurity atom. The present calculations consider all electrons; neither the frozen-core nor the muffin-tin approximations were made. An auxiliary fit to the charge

density was needed, in the calculations of the matrix elements of the Coulomb potential, due to the enormous number of two-electron integrals one must otherwise evaluate. This fit<sup>26</sup> involved separate basis sets of 14 *s* and 9 *p* functions for each atom. A more complete description of the method employed can be found in Ref. 20.

### III. RESULTS

#### A. General remarks

The present calculations supplement those reported in Ref. 23, and enable a rather complete picture of the electronic structure of 3*d* elements in Cu to be derived. In the discussions below, we use the term "up" to refer to electrons of spin parallel to those of the majority, and similarly "down" refers to the minority.

In a general way, the changes in the density of states as the atomic number of the impurity varies from that of chromium to that of nickel can be viewed as the passage first of an up-spin peak in the density of states below the Fermi level, and then, beginning with Fe, the passage of a down-spin peak. At or above the Fermi level, the impurity density-of-states peak is fairly sharp; but below the Fermi energy, the peak becomes broader, presumably because of hybridization with the Cu *d* band. This broadening of the impurity density of states when there is a possibility of hybridization with host *d* states distinguishes the present results from previous studies.

#### B. Cu<sub>18</sub>Cr

Figure 1 exhibits the electronic energy levels of this system. We know of no previous publication of the calculated electronic structure of Cu<sub>18</sub>Cr clusters. The distribution of the levels about the Fermi energy, which coincides

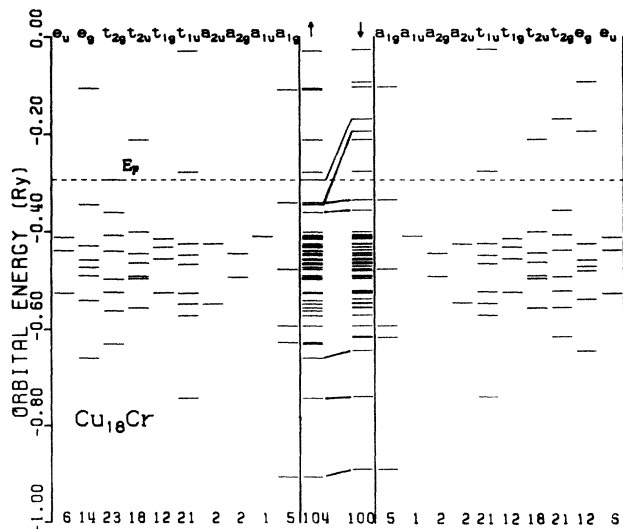


FIG. 1. Energy-level diagram for the Cu<sub>18</sub>Cr cluster for up and down spins. Some levels are connected by a line, to illustrate the spin splitting.

with an up-spin *t*<sub>2g</sub> state, is of particular interest. The next occupied levels, closest to *E*<sub>F</sub>, are the down- and up-spin *a*<sub>1g</sub> levels and the up-spin *e*<sub>g</sub> level, respectively, at 0.57, 0.65, and 0.70 eV below *E*<sub>F</sub> while the up- and down-spin *t*<sub>1u</sub> levels are, respectively, 0.21 and 0.24 eV above *E*<sub>F</sub>. The predicted optical transition energies, from the lowest valence *e*<sub>g</sub> and *t*<sub>2g</sub> states to the aforementioned *t*<sub>1u</sub> levels of like spin are, respectively, 5.18 and 4.99 eV for the up and down spin *e*<sub>g</sub>, 4.79 and 4.60 eV for the up and down *t*<sub>2g</sub>.

An important feature of this electronic structure stems from the fact that the *t*<sub>2g</sub> state at the Fermi level and the occupied up-spin *e*<sub>g</sub> state closest to *E*<sub>F</sub> are both impurity levels, insofar as one can ascribe a level to a site in this complex system. This is in agreement with expectations inferred from incremental residual resistivity maximum for Cr in aluminum as compared to other 3*d* impurities. This has been discussed by Kondo<sup>10</sup> in terms of a maximum influence of the impurity states at the Fermi level for chromium in copper. We find, in qualitative agreement with the results of Johnson and collaborators,<sup>19</sup> that there is an impurity *a*<sub>1g</sub> state at the bottom of the level complex, while in the middle are the Cu *d*-like states which are not much changed from those of a Cu<sub>19</sub> cluster.

The largest exchange splittings are, respectively, 2.06 and 1.70 eV for the *e*<sub>g</sub> and *t*<sub>2g</sub> states as indicated in Fig. 1. The splitting for copper *d* levels, as can be estimated from Fig. 1, is rather small as expected. The cluster densities of states (CDOS) are presented in Fig. 2. One should note the difference of the scales for the central (impurity) and the first- or second-shell contributions.

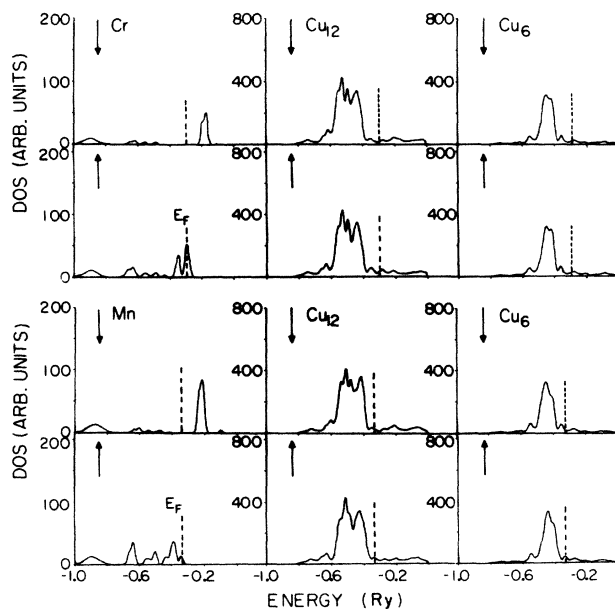


FIG. 2. Cluster density of states (CDOS) for Cu<sub>18</sub>Cr and Cu<sub>18</sub>Mn clusters. For each cluster the upper curve is for the down spin. Note the difference between the scales used for the impurity atom contribution and that of the copper atoms. The levels have been broadened as described in the text.

TABLE I. Mulliken population analysis from integrated CDOS ( $M$  stands for the central atom).

	Cu <sub>18</sub> Cr	Cu <sub>18</sub> Mn
$M$ $sp$ $\uparrow$	1.18	1.17
$M$ $sp$ $\downarrow$	1.24	1.24
$M$ $d$ $\uparrow$	4.20	4.83
$M$ $d$ $\downarrow$	0.67	0.79
$M$ tot	7.29	8.03
Cu <sub>12</sub> $sp$ $\uparrow$	0.64	0.66
Cu <sub>12</sub> $sp$ $\downarrow$	0.62	0.62
Cu <sub>12</sub> $d$ $\uparrow$	4.89	4.88
Cu <sub>12</sub> $d$ $\downarrow$	4.85	4.84
Cu <sub>12</sub> tot	11.00	11.00
Cu <sub>6</sub> $sp$ $\uparrow$	0.51	0.53
Cu <sub>6</sub> $sp$ $\downarrow$	0.50	0.53
Cu <sub>6</sub> $d$ $\uparrow$	4.88	4.88
Cu <sub>6</sub> $d$ $\downarrow$	4.87	4.88
Cu <sub>6</sub> tot	10.76	10.82

These curves are produced by broadening of the energy levels with Gaussians of widths 0.6 eV for  $s$ - and  $p$ -type states and 0.15 eV for  $d$  levels. The CDOS curves for Cu<sub>18</sub>Cr illustrate the level distributions as well as the exchange splitting discussed above. The chromium and copper  $d$  levels do not overlap much as the former are closer to the Fermi level. As far as the peaks are concerned the CDOS for the first- and second-shell copper atoms resemble the results of Blaha and Callaway<sup>23</sup> for Cu<sub>18</sub>Fe. These authors, who also studied Cu<sub>18</sub>Cu, compared copper CDOS to the band-structure calculation results of Bagayoko<sup>27</sup> *et al.*<sup>28</sup> While the first-shell contributions are found to agree with the bulk results, the second shell CDOS, which has a simple peak, can be described as a surface density of states roughly similar to that found by Delley *et al.*<sup>29</sup> in Cu<sub>79</sub> clusters. These conclusions hold also for Cu<sub>18</sub>Cr. The splitting of the up-spin Cr peak at  $E_F$  and the empty down-spin one is about 2.06 eV. This compares favorably with the 2.17 eV finding of the KKR Green's function calculations. However, there is an important qualitative difference between the cluster CDOS presented here and the KKR results.<sup>17-19</sup> Braspenning *et al.*<sup>19</sup> found an up-spin peak at  $E_F$  for a vanadium impurity instead of for chromium as is the case here. We have a two-peak structure whereas the KKR results show only one for the majority spin. Our result can be regarded as showing the cubic field splitting of the Cr  $d$  states; however, this type of structure is sensitive to the somewhat arbitrary broadening we have introduced.

The cluster magnetic moment is  $4.0\mu_B$  with  $3.53\mu_B$  from impurity  $d$  contributions as can be seen in Table I

TABLE II. Spin density at the nuclei (in  $e/a.u.^3$ ).

	Cu <sub>18</sub> Cr	Cu <sub>18</sub> Mn
$M$	-0.211	-0.262
Cu <sub>12</sub>	-0.086	-0.005
Cu <sub>6</sub>	0.073	0.057

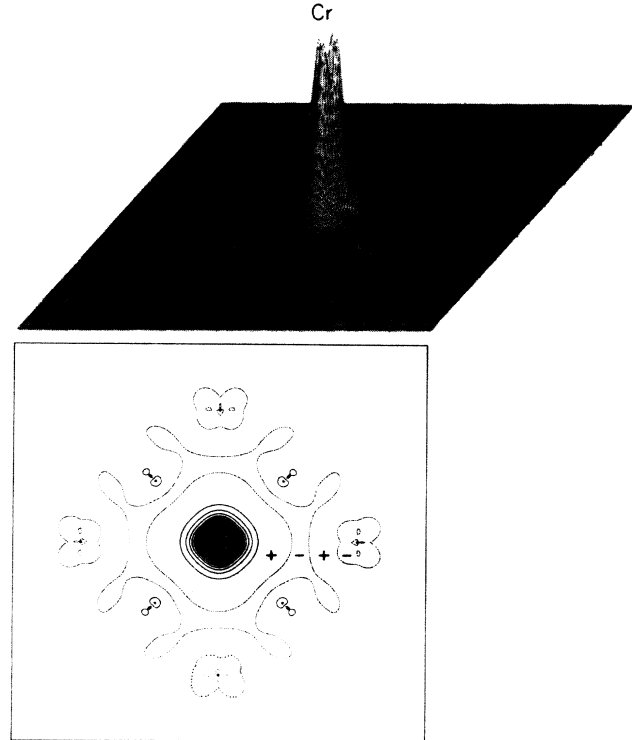


FIG. 3. Spin-density distribution of Cu<sub>18</sub>Cr in the (100) plane. Zero at dashed lines, lowest contour at  $0.025 e/a.u.^3$ , adjacent lines differ by a factor of 2.

where the results of the Mulliken population analysis are reported. This type of analysis, which is of qualitative usefulness only, leads to a total moment of  $4.21\mu_B$  which is unphysically larger than the directly computed  $4.0\mu_B$ . The local moment of  $3.53\mu_B$  compares fairly well with the experimental<sup>8</sup> result of  $3.3\mu_B$ . Table II indicates a negative spin density at the nuclear sites of the impurity and first-shell copper atoms, while a positive value is obtained for the second-shell Cu sites. The valence-electron deficit in the second shell is compensated by the excess on the impurity. The magnetic polarization of copper  $d$  states is about  $0.04\mu_B$  and  $0.01\mu_B$  per first- and second-shell atoms, respectively. Three-dimensional and contour plots of the spin-density distribution are shown in Fig. 3. The impurity atom is surrounded by a region of negative spin polarization primarily involving  $s$ - $p$  electrons. In this respect we see a weak antiferromagnetic coupling of the  $s$ - $p$  electrons with the impurity  $d$  electrons, as in the theory of the Kondo effect. In these density functional calculations, the screening of the local moment results from a tendency discussed in Ref. 22 toward spatial segregation of electrons of opposite spins. However, we see from Table I that the screening is fairly weak.

### C. Cu<sub>18</sub>Mn

The electronic energy levels of this cluster are shown in Fig. 4. The Fermi level falls on a down-spin  $a_{1g}$  state with up-spin  $t_{2g}$  and  $a_{1g}$  states at, respectively, 0.087 and 0.102 eV below it. In the calculation of Ref. 19, these lev-

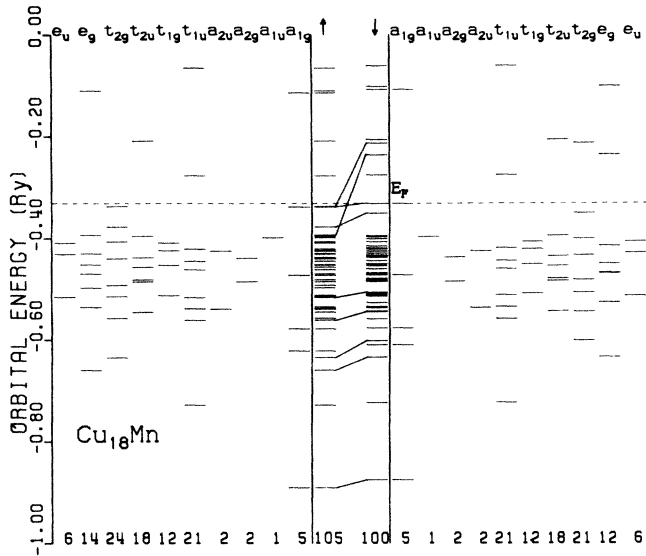


FIG. 4. Energy-level diagram for the  $\text{Cu}_{18}\text{Mn}$  cluster for up and down spins. Some levels are connected by a line, to illustrate the spin splitting.

els are also close to the Fermi energy but we do not find  $e_g$  levels particularly close to  $E_F$ . No impurity  $d$  level lies at the Fermi energy contrary to the case for Cr. The unoccupied states closest to  $E_F$  are of  $t_{1u}$  symmetry. They are, respectively, 0.74 and 0.77 eV above  $E_F$  for the up and down spins. Transitions from the lowest valence  $e_g$  levels to these  $t_{1u}$  levels, respectively, require 5.20 and 4.88 eV for up and down spins. No spin flip is considered; the average transition energy is therefore 5.04 eV in excellent agreement with experiment<sup>30</sup> which finds 5.0 eV. The optical transition energies between the lowest valence  $t_{2g}$  and the aforementioned  $t_{1u}$  levels are 4.86 and 4.44 eV for up and down spins, respectively. The largest exchange splittings are, respectively, 2.16 and 1.7 eV between the highest occupied up-spin  $e_g$  and  $t_{2g}$  and their corresponding down- (empty) spin levels. These values are an order of magnitude larger than the results of Johnson *et al.*

A major difference between Cr and Mn is the substantial overlap, for the latter, of the impurity  $d$  levels and those of the copper hosts. This is apparent from Fig. 2 which shows the CDOS for both systems. The up-spin CDOS  $d$  contribution from first-shell atoms is mixed with and is sandwiched between the peaks of the corresponding contributions from manganese. These CDOS curves have been broadened as described for  $\text{Cu}_{18}\text{Cr}$ . The cluster magnetic moment is  $5.0\mu_B$  for  $\text{Cu}_{18}\text{Mn}$  with  $4.04\mu_B$  of it due to Mn  $d$  electron contribution (Table I). This local moment is in excellent agreement with the experimental value of  $4.02\mu_B$  of Hurd.<sup>31</sup> This agreement is particularly significant in light of the precautions taken by Hurd, who used dilute alloys to minimize impurity-impurity interaction. The Mulliken population analysis results, in Table I, again indicate  $s$ - $p$  spin compensation clouds about the impurity. The same remarks apply here as in the case of a chromium impurity. There is no  $d$  polarization for the

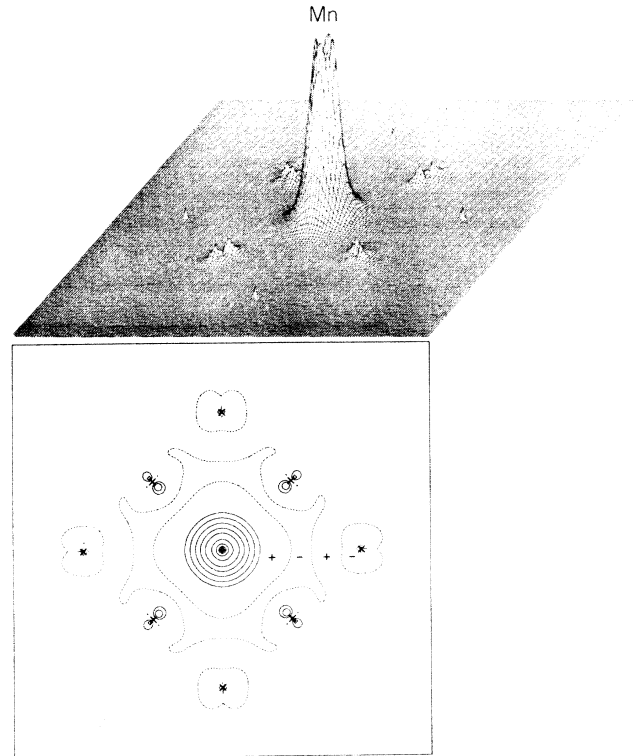


FIG. 5. Spin-density distribution of  $\text{Cu}_{18}\text{Mn}$  in the (100) plane. Zero at dashed lines, lowest contour at  $0.025 e\text{-a.u.}^3$ , adjacent lines differ by a factor of 2. The crosses indicate Cu atom sites.

second-shell Cu atoms. For the first-shell atom we have  $0.04\mu_B$   $d$  polarization per atom.  $\text{Cu}_{18}\text{Mn}$  exhibits negative spin density at the impurity and first-shell copper atom nuclei as shown in Table II and Fig. 5.

#### IV. CONCLUSION

We have presented the electronic structure of Cr and Mn impurities in copper. Our self-consistent calculations employed a local-spin-density potential and Gaussian orbitals in a LCGO procedure applied to the free clusters  $\text{Cu}_{18}\text{Cr}$  and  $\text{Cu}_{18}\text{Mn}$ . This work complements that of Blaha and Callaway and leads to a general picture of the electronic structure of  $3d$  impurities in copper. For Cr in Cu the impurity local moment of  $3.53\mu_B$  is reasonably close to the experimental value of  $3.3\mu_B$ . The largest exchange splitting obtained is 2.06 eV. The CDOS curves exhibit two peaks, one of which is at the Fermi level, for the majority spin. This result is different from the findings of the KKR calculations. We have predicted several optical transition energies. In the case of Mn in Cu a local impurity moment of  $4.04\mu_B$  was found. This is in excellent agreement with the experimental value of  $4.02\mu_B$  as obtained by Hurd. The largest exchange splitting is 2.16 eV. We reproduced the experimental optical transition energy of 5.0 eV.

An interesting general feature of these and our previous calculations is that the total cluster moment is found to be equal to that of the isolated impurity atom in each case.

This appears in both the work of Blaha and Callaway and the present results. The cluster moment contains contributions from spin polarization of host atoms which supplement the local impurity moment. Moreover, the exchange splittings of the impurity states are not small.

As the atomic number of the impurity increases, from 24 for Cr to 28 for Ni, impurity peaks in the CDOS curves move below the Fermi level. The passage of an up-spin peak occurs for Cr while that of a down-spin peak takes place for Fe. The descent of a peak below the Fermi level is accompanied by its broadening.

These investigations were undertaken in part to see whether the rather surprising conclusions of Ref. 19 relating cluster calculations using the  $X\alpha$  approximation and the scattered wave method would hold when the calculations were repeated by methods we believe to be more powerful. This problem is of considerable significance in

regard to the use of clusters to simulate impurity problems in solids. Authors who have studied systems of this type using methods more obviously appropriate for solids (e.g., KKR) and have not found agreement with Ref. 19 have concluded that cluster methods are inappropriate. We believe that these calculations, which give results generally much closer to those of the KKR approach rather than to the  $X\alpha$ -scattered wave method, indicate that conclusion was premature, and that cluster calculations can give a reasonable description of magnetic impurities in copper (subject, of course, to the general limitations of spin-density functional theory in the local approximation).

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\*Also at Department of Physics, Southern University, Baton Rouge, LA 70813.

†Permanent address: Institut für Technische Elektrochemie TU-Wien Getreidemarkt 9, A-1060 Wien Austria.

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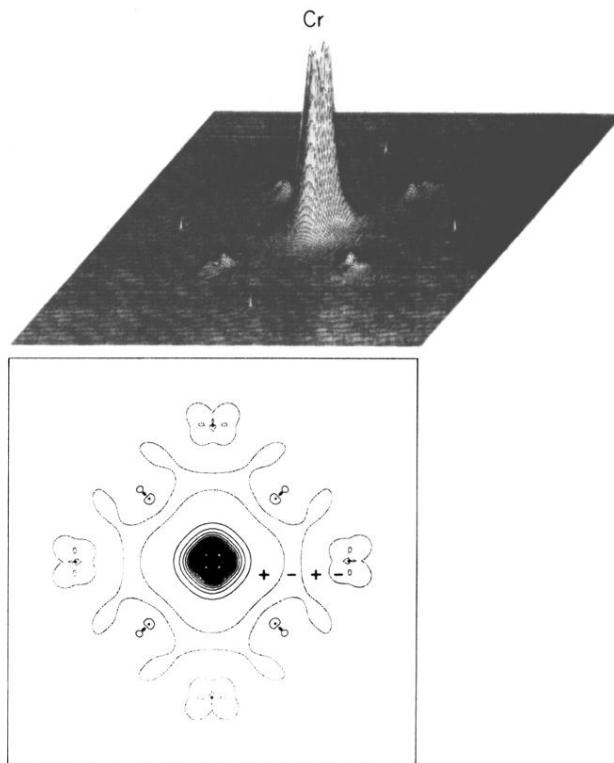


FIG. 3. Spin-density distribution of  $\text{Cu}_{18}\text{Cr}$  in the (100) plane. Zero at dashed lines, lowest contour at  $0.025 \text{ e/a.u.}^3$ , adjacent lines differ by a factor of 2.

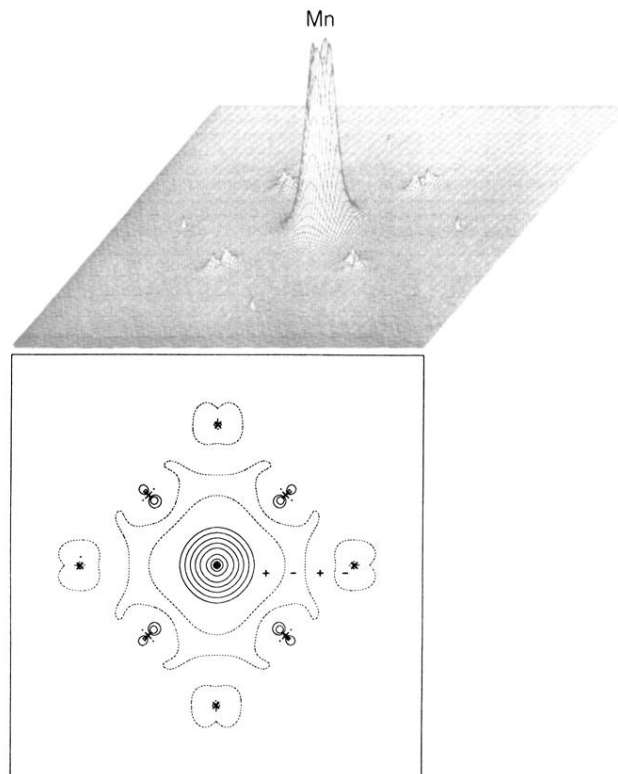


FIG. 5. Spin-density distribution of  $\text{Cu}_{18}\text{Mn}$  in the (100) plane. Zero at dashed lines, lowest contour at  $0.025 \text{ e-a.u.}^3$ , adjacent lines differ by a factor of 2. The crosses indicate Cu atom sites.