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Electronic structure and magnetic properties of 3*d* impurities in ferromagnetic metals

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The electronic structure of 3*d* impurities (from Ti to Ni) in ferromagnetic metals (bcc and fcc Fe, hcp and fcc Co, fcc Ni) is calculated by the linear-muffin-tin-orbital Green's-function method. The values of local magnetic moments and effective exchange parameters are listed. For Mn impurities in bcc Fe and hcp Co, two possible impurity configurations with different spin direction are found. Based on the analysis of effective exchange parameters, the relative stability of different configurations is discussed.

I. INTRODUCTION

Ferromagnet (Fe, Co, Ni)-based alloys, because of peculiar types of magnetic behavior they exhibit, have been widely studied, both experimentally and theoretically. For the understanding of the concentration-dependent tendencies in the electronic structure of these alloys, the study of single transition metal (TM) impurities in ferromagnets is of vital importance. Since the impurity atoms in these systems always carry a local magnetic moment (an induced one, if not their own), the magnitude and direction of this magnetic moment, along with the strength of its coupling to the spins of host metal atoms, are first of all to be specified.

The most common rule is that the early-TM impurities (Ti, V) carry antiparallel magnetic moments with respect to those of host metal atoms while in the middle of a TM-series the inversion of impurity magnetic moment to parallel orientation takes place. The situation is least understood for the intermediate 3*d* impurities for which a variety of contradictory experimental data have been reported (see Ref. 1 for the review of experimental situation). For example, nonpolarized neutron diffraction measurements for *Fe*Mn alloys give values of a Mn local moment from $0.0\pm0.2\mu_B$ (Ref. 2) to $1.0\pm0.2\mu_B$ (Ref. 3), while in recent polarized neutron diffraction measurements both parallel [$0.77\mu_B$ (Ref. 4)] and antiparallel [$-0.82\mu_B$ (Ref. 5)] orientations of a Mn local magnetic moment in these alloys have been found. Exact experimental determination of the value of the Mn impurity magnetic moment is complicated by its pronounced concentration[5] and temperature[3] dependence in *Fe*Mn alloys.

For 3*d* impurities in Ni, a jump from antiparallel to parallel orientation of the impurity moment takes place undoubtedly between Cr and Mn,[2] the value of a Mn impurity magnetic moment being $2.4\pm0.1\mu_B$, according to Ref. 2, or $3.50\pm0.13\mu_B$, according to Ref. 6 (both are nonpolarized neutron scattering data). It is worth noting that the impurity magnetic moment in the *Ni*Mn system depends considerably on the local environment.[6]

For 3*d* impurities in Co, an interesting point is that they can exhibit different behavior when embedded into hcp or fcc phases of the host metal (both of which are obtainable at room temperature). For example, the NMR data on *Co*Mn alloys[7] reveal the ferromagnetic (parallel) coupling between magnetic moments of Co and Mn atoms in fcc samples and antiferromagnetic coupling in hcp samples, with rough estimates for the local moment as $3.3\mu_B$ and $-3.2\mu_B$, respectively. The last result was supported qualitatively by polarized-neutron diffraction study of hcp *Co*Mn alloys that gave an impurity moment of $-0.53\mu_B$ (Ref. 8) for the lowest concentration studied (5 at % Mn).

Although the change of impurity moment orientation when going along the TM series can be understood qualitatively on the basis of the rather simple two-impurity model,[9] the influence of a given crystal phase and specific electronic structure of the host on magnetic properties of impurities can be explained only with the help of a numerical first-principles calculation. Since the Korringa-Kohn-Rostoker KKR-Green's function formalism for impurities in infinite crystals has been proposed and proven to be feasible,[10] numerous works have appeared devoted to TM impurities, e.g., those in ferromagnetic iron[11-13] and nickel.[14-16] In the more recent of these papers,[12,15,16] potentials of atoms surrounding the impurity were allowed to change towards complete self-consistency. Therefore, the charge transfer has been taken properly into account. However, no calculations have appeared so far for 3*d* impurities in cobalt and fcc iron. The aim of this paper is to present the calculated results for these systems. As a first step, we consider the perturbation of the potential only at the impurity site. Along with the easily obtainable values of spin magnetic moments, we concentrate on the parameters of effective impurity-host exchange interaction. These parameters, which determine the direction of the impurity magnetic moment and its stability with respect to small deviation, have not been reported so far, even for well-studied Fe- and Ni-based systems. Therefore, we have performed self-consistent impurity calculations for these systems as well.

II. METHOD OF CALCULATION

The electronic structure of pure host metals has been determined self-consistently by the linear-muffin-tin-orbital (LMTO) atomic-sphere-approximation (ASA), method.[17] The electronic structure of the impurity system was then found by means of the LMTO–Green's-function method[18] (see also Ref. 19). In the atomic sphere approximation, the Green's function of crystal takes the form

$$G(\mathbf{R}_n+\mathbf{r},\mathbf{R}_{n'}+\mathbf{r}',\varepsilon)=\sum_{L,L'}R_{nl}(|\mathbf{r}|)Y_L(\hat{\mathbf{r}})\dot{p}_{nl}^{1/2}(\varepsilon)T_{LL'}^{nn'}(\varepsilon)\dot{p}_{n'l'}^{1/2}(\varepsilon)Y_{L'}(\hat{\mathbf{r}}')R_{n'l'}(|\mathbf{r}'|)$$
$$-\delta_{nn'}\sum_{L}R_{nl}(|\mathbf{r}|)Y_L(\hat{\mathbf{r}})\left[\frac{\dot{p}_{nl}(\varepsilon)}{p_{nl}(\varepsilon)}-\frac{1}{\varepsilon-\varepsilon_{nl}^{*}}\right]Y_L(\hat{\mathbf{r}})R_{nl}(|\mathbf{r}|)\ , \qquad (1)$$

where n,n' are site indices, $L\equiv(l,m)$, and $R_{nl}(|\mathbf{r}|)$ is a regular (at $r=0$) solution of the radial Schrödinger equation in nth atomic sphere at fixed energy $\varepsilon=\varepsilon_{\nu nl}$. $p_{nl}(\varepsilon)$ is the so-called potential function

$$p_{nl}(\varepsilon)=2(2l+1)\frac{D_{nl}+l+1}{D_{nl}-l}\ , \qquad (2)$$

where D_{nl} is a logarithmic derivative of the radial solution $R_{nl}(r)$ at the atomic-sphere boundary. The dot over $p_{nl}(\varepsilon)$ means the energy derivative and ε_{nl}^{*} is a root of the potential function. For a perfect crystal, the scattering path operator $T_{LL'}^{nn'}(\varepsilon)$ can be found as follows:

$$T_{LL'}^{nn'}(\varepsilon)=\frac{1}{\Omega}\int_{BZ}d\mathbf{k}[p(\varepsilon)-S(\mathbf{k})]_{LL'}^{-1}$$
$$\times\exp[i\mathbf{k}(\mathbf{R}_n-\mathbf{R}_{n'})]\ . \qquad (3)$$

Here, $S(\mathbf{k})$ are energy-independent structure constants of the LMTO method.

When potentials are disturbed at a finite number of sites, a scattering path operator for a defect crystal can be found through the following matrix identity:

$$\underline{\tilde{T}}=\underline{T}[\underline{1}+(\underline{\tilde{p}}-\underline{p})\underline{T}]^{-1}\ , \qquad (4)$$

where matrices $\underline{p}$ are diagonal in n and l. For a special case of a single disturbed potential in a crystal of cubic point symmetry, matrix identity (4) results in an extremely simple scalar form for diagonal elements of $\underline{\tilde{T}}$ (for $l\leq 2$)

$$\tilde{T}_{LL}^{nn}=\frac{T_{LL}^{nn}}{1+(\tilde{p}_{nl}-p_{nl})T_{LL}^{nn}}\ . \qquad (5)$$

In other cases, it is not exactly true. However, we applied this formula to impurities in hexagonal Co, neglecting off-diagonal (in l) elements of $T_{LL'}^{nn}$ which were actually small in the whole energy range of interest.

In the course of the iterative procedure for an impurity system, partial state populations were determined with good accuracy by the complex energy integration of the Green's function.[20] Although potentials on neighboring sites were not changed, possible effects of improper treatment of the charge transfer were, to a certain extent, amended by the adjustment of the radius of the impurity sphere during the iterations in order to maintain its charge neutrality.

For the local spin moment at the impurity site, we used the expression

$$M=\int^{\varepsilon_F}d\varepsilon[n_{\uparrow}(\varepsilon)-n_{\downarrow}(\varepsilon)]\ , \qquad (6)$$

where

$$n_{\sigma}(\varepsilon)=-\frac{1}{\pi}\int d\mathbf{r}\,\mathrm{Im}G_{\sigma}(\mathbf{r},\mathbf{r},\varepsilon)\ , \qquad (7)$$

the integration being over the impurity atomic sphere. The exchange-correlation potential of Gunnarsson and Lundqvist[21] was used throughout.

An expression for the exchange parameter in terms of single-site T matrices has been derived in Ref. 22:

$$J_0=-\frac{1}{4\pi}\int^{\varepsilon_F}d\varepsilon\,\mathrm{Im}\,\mathrm{Tr}[\Delta_0(\tilde{T}_{\uparrow}^{00}-\tilde{T}_{\downarrow}^{00})$$
$$+\Delta_0\tilde{T}_{\uparrow}^{00}\Delta_0\tilde{T}_{\downarrow}^{00}]\ . \qquad (8)$$

Here, $\Delta_0=\tilde{p}_{0\uparrow}-\tilde{p}_{0\downarrow}$, and trace is taken over orbital variables. In the limit of completely localized moments, this parameter has the following analog in the Heisenberg model:

$$J_0=\sum_{j\neq 0}J_{0j}\frac{\mathbf{M}_0\cdot\mathbf{M}_j}{|\mathbf{M}_0|\ |\mathbf{M}_j|}\ . \qquad (9)$$

Therefore, it is always positive in the ground state of the spin system. In a pure ferromagnet, the Curie temperature is closely related to J_0.[23] When calculated for an impurity system or a magnetic atom in a disordered alloy, J_0 can be found to be negative. This means that a given

TABLE I. Calculated values of local magnetic moments and effective exchange parameters for $3d$ impurities in ferromagnetic metals.

Impurities:	Ti	V	Cr	$\mathrm{Mn}_\downarrow$	$\mathrm{Mn}_\uparrow$	$\mathrm{Fe}_\downarrow$	$\mathrm{Fe}_\uparrow$	Co	Ni
				(in bcc Fe)					
M (μ_B)	−0.82	−1.13	−1.60	−2.30	1.60		2.25	1.49	0.73
J_0 (mRy)	1.2	2.9	12.4	9.3	1.5		17.1	15.4	7.9
				(in fcc Fe)					
M (μ_B)	−0.90	−1.36	−2.26	−2.96	2.48	−2.72	2.43	1.22	0.56
J_0 (mRy)	1.3	10.9	16.0	12.1	−7.2	−0.7	11.2	8.9	4.6
				(in hcp Co)					
M (μ_B)	−0.52	−0.90	−1.73	−2.73	2.03	−2.40	2.48	1.51	0.62
J_0 (mRy)	2.4	5.4	10.2	10.1	5.3	−17.0	15.3	13.5	5.8
				(in fcc Co)					
M (μ_B)	−0.50	−1.16	−1.78	−2.88	2.66	−2.31	2.50	1.49	0.62
J_0 (mRy)	2.1	8.1	10.6	−2.7	12.6	−28.4	15.3	14.7	5.8
				(in fcc Ni)					
M (μ_B)	−0.11	−0.42	−0.79	−2.87	2.89	−3.10	2.72	1.51	0.62
J_0 (mRy)	0.2	1.2	1.8	−4.6	8.8	−18.0	11.6	9.3	2.9

spin configuration is unstable with respect to small spin deviations.[22]

It is possible that the spin configuration found as a result of a self-consistent calculation appears to be unstable in this sense, because only the magnitude of the magnetic moment, and not its direction, is allowed to vary in usual spin-polarized calculations. Therefore, every self-consistent solution corresponds to a conditional minimum of the total energy, which, however, may not be an absolute one.

III. RESULTS AND DISCUSSION

Calculated densities of states for $3d$ impurities in Fe (bcc and fcc), Co (hcp and fcc), and Ni are shown in Figs. 1–5, respectively. The values of impurity local moments and the exchange parameters are given in Table I. In our calculations, experimentally found lattice parameters (see, e.g., Ref. 24) were used for all ferromagnetic metals but one. For γ-Fe(fcc), a lattice constant $a = 6.88$ a.u. has been taken, as it has been found in Ref. 25 to correspond to the high-spin ferromagnetic state of fcc Fe.

It is a common feature of all TM-based impurity systems that strong hybridization between $3d$ states of impurity and host takes place, resulting in a rather complicated local density of states at the impurity site. For the early $3d$ impurities, pronounced virtual bound states of Lorentzian-like shape are visible above the Fermi level, roughly revealing the initial energy position of an impurity $3d$ eigenstate. What can be seen below the Fermi level is the result of the admixture of impurity $3d$ states in the conduction band of the host metal. The admixture in the spin-down host states is more pronounced since they are shifted up in energy nearer to the impurity level due to the ferromagnetic splitting of the conduction band. Therefore, spin-down states at the impurity site are more

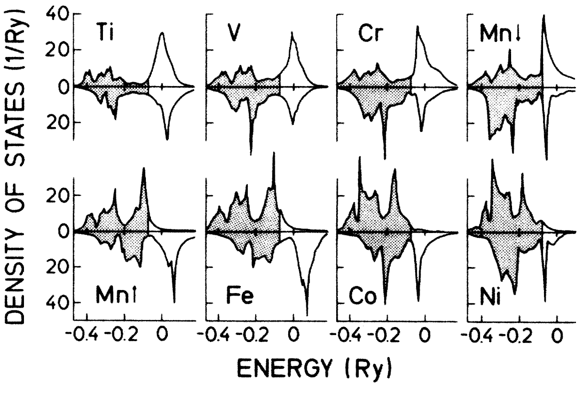

FIG. 1. Local densities of states for $3d$ impurities in bcc Fe.

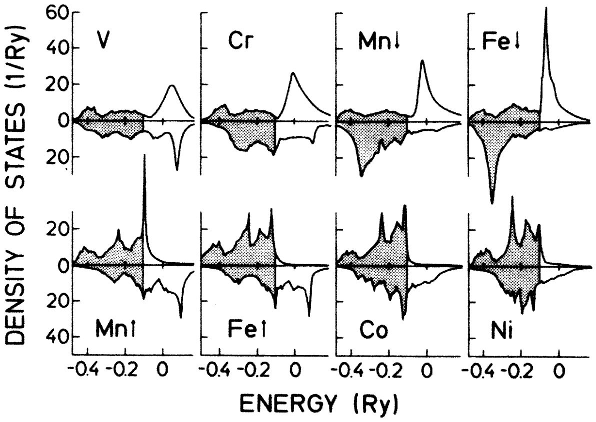

FIG. 2. Local densities of states for $3d$ impurities in fcc Fe.

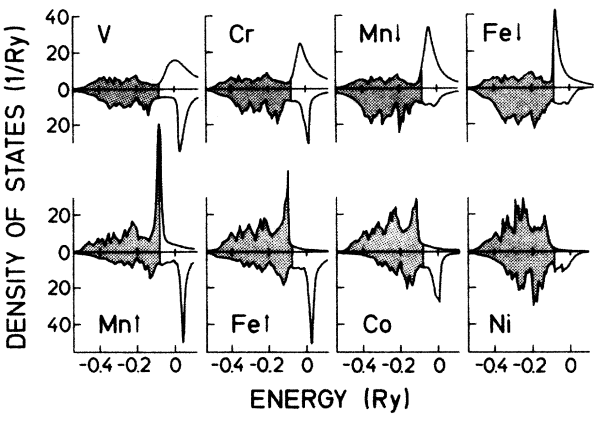

FIG. 3. Local densities of states for 3*d* impurities in hcp Co.

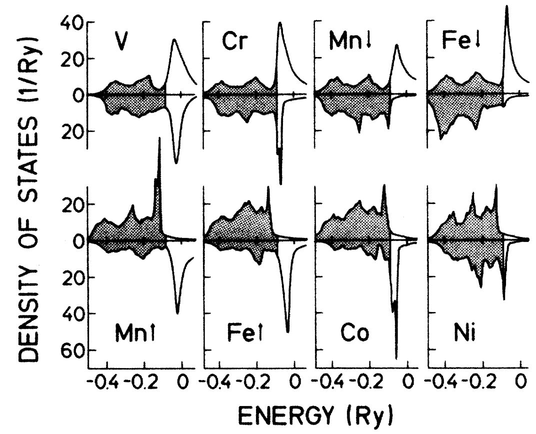

FIG. 5. Local densities of states for 3*d* impurities in fcc Ni.

populated; that means the impurity magnetic moment is inverted with respect to the host magnetization. For subsequent impurities, the initial 3*d* level goes gradually below the Fermi energy, the virtual bound state dissolves in the conduction band, and the fact that the occupied part of a spin-up (majority) sub-band is more broad in energy, results in the preferential population of spin-up states at the impurity site and, hence, ferromagnetic orientation of the impurity moment.

It is the main tendency around which some minor variations in the middle of a 3*d* series are possible. When performing the calculations, we looked for both parallel and antiparallel self-consistent solutions for the impurity moment in all cases, starting from different initial conditions. Only for Mn and Fe impurities have these twin solutions been actually found (see Table I). Although self-consistent with respect to the usual spin-polarized calculations, many of these solutions must be eliminated as unstable with respect to small spin deviations in cases when the exchange parameter J_0 is negative. So, only ferromagnetic solutions must be retained for Fe impurities in all host metals and for Mn impurities in fcc Co and Ni. The magnetic moment of the Mn impurity in fcc Fe undoubtedly tends to be directed antiparallel to the host magnetization. Two other cases (Mn in bcc Fe and hcp Co) need special discussion.

In principle, both solutions in each of these cases correspond to energy minima, and the accurate comparison of total energies (that is rather complicated for impurity systems) is necessary to indicate the true ground state. It can be expected (although not proven), however, that a larger value of J_0 (which is, roughly speaking, the second derivative of the energy with respect to deviations; see Ref. 22) corresponds to a deeper minimum of total energy. This consideration favors the antiparallel orientation of the Mn impurity in bcc Fe, in agreement with the ex-

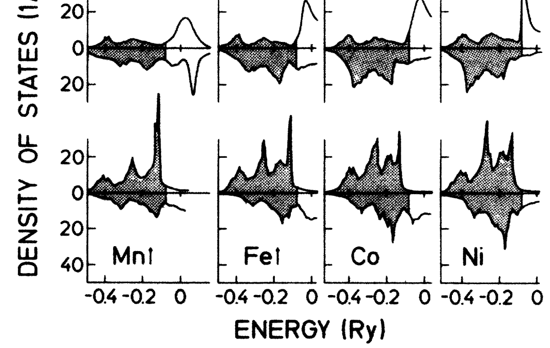

FIG. 4. Local densities of states for 3*d* impurities in fcc Co.

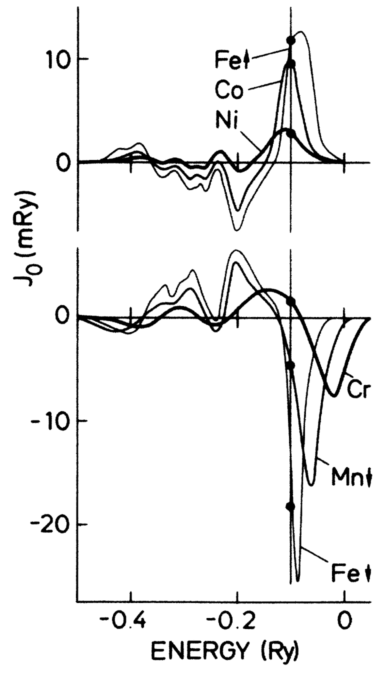

FIG. 6. Effective exchange parameter J_0 [Eq. (8)] as function of ϵ_F for some impurities in Ni. The actual position of ϵ_F is indicated by a vertical line.

perimental data chosen for comparison in Refs. 12 and 13 to support a similar result obtained in these calculations.

It was emphasized in Ref. 13 that direction of a Mn impurity moment is very sensitive to slight changes of the impurity potential and that under continuous change of impurity nuclear charge a jump from antiparallel to parallel orientation occurs in a rather narrow region, $25.16 < Z < 25.18$, close to the actual value for Mn.

Taking into account that the opposite direction of a Mn impurity moment is also at least metastable according to the present calculation, a variety of contradictory experimental data cited in the Introduction can be understood as a result of fluctuations between two possible configurations in a real system.

For a Mn impurity in hcp Co, similar consideration favors the more stable antiparallel orientation, in contrast to the situation in fcc Co where only parallel orientation is allowed. Therefore, the experimental evidence[7] strongly supports our results for the *Co*Mn system. Since net spin moments are not available from most of the experimental data, a quantitative comparison between theory and experiment is not always possible.

When compared to previous calculations for impurities in Fe and Ni,[12–14] our results exhibit, as a whole, rather good agreement (within $\pm 0.2\mu_B$) in determined values of local magnetic moments. The worst agreement is for Mn in bcc Fe (the magnetic moment is about $-1.7\mu_B$, according to Ref. 13) and for Cr in Ni [$\mu = -1.3\mu_B$ (Ref. 14)]. The magnetic moments in these two systems have been reported to be especially sensitive to small variations in the potential used in the calculation.[13,15] The source of disagreement between our calculation and earlier ones may result from the different schemes for the exchange-correlation potential that are used. In addition, the treatment of the spatial distribution of the potential in the atomic-sphere approximation (the present calculation) is different from the treatment in the muffin-tin approximation used in Refs. 13–15.

For other systems, the only calculated data available are those concerning pure metals; magnetic moments listed in Table I for self-substituting impurities are in fairly good agreement with results of band structure calculations for fcc Fe,[26] hcp Co,[27] and fcc Co.[28]

The last question concerns the sensitivity of the exchange parameter J_0 calculated by Eq. (8) for small perturbations of the electronic structure. For illustrative purposes, J_0 as a function of the upper integration limit in (8) is presented in Fig. 6 for several impurities in nickel. One can see that $J_0(\epsilon_F)$ is a rather smooth function which, however, changes sign several times when passing through the d band. When the actual position of the Fermi level falls into one of these critical regions, considerable uncertainty in the value of J_0 can result from less accurate calculations.

IV. CONCLUSION

In this work, we have presented the results of LMTO–Green's-function calculations for $3d$ impurities in all known pure ferromagnetic metals. Combined use of self-consistent spin-polarized results and calculated effective exchange parameters has enabled us to discuss the relative stability of different spin configurations and to gain some insight into sometimes contradictory experimental data.

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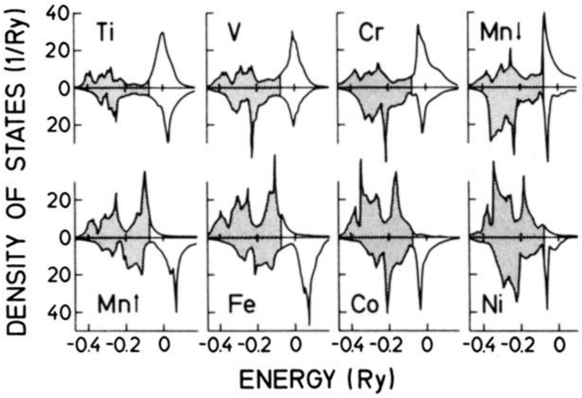

FIG. 1. Local densities of states for 3*d* impurities in bcc Fe.

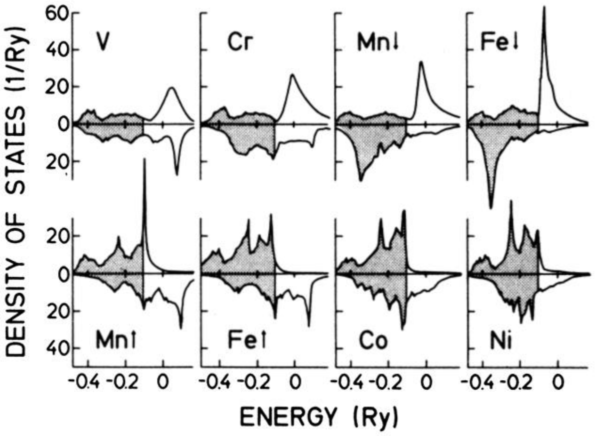

FIG. 2. Local densities of states for 3*d* impurities in fcc Fe.

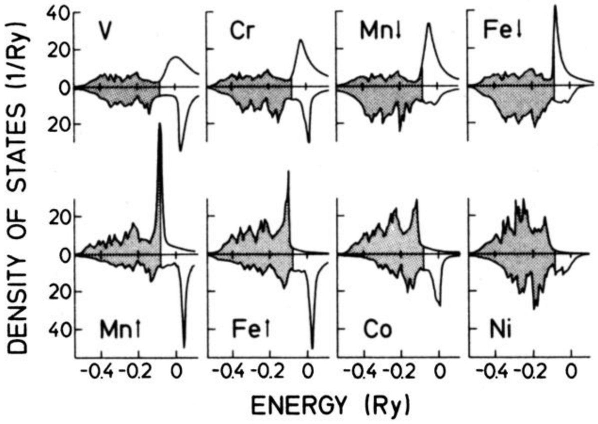

FIG. 3. Local densities of states for 3*d* impurities in hcp Co.

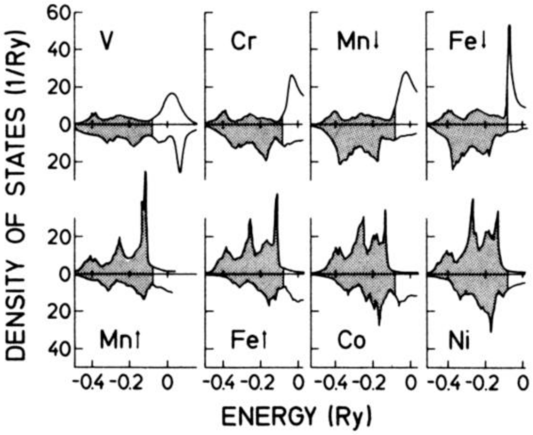

FIG. 4. Local densities of states for 3*d* impurities in fcc Co.

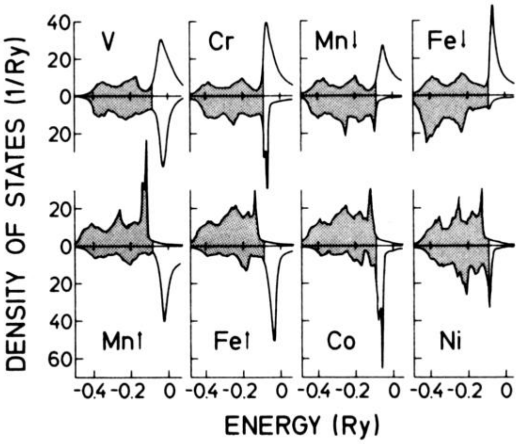

FIG. 5. Local densities of states for 3*d* impurities in fcc Ni.