*Asian Journal of Chemistry* Vol. 18, No. 5 (2006), 3286-3291

# Spin Density and Magnetic Moments on Impurities in Ni and Pd Metals

J. SINGH
*Department of Mathematics, Statistics and Physics, Punjab Agricultural University, Ludhiana-141 004, India*
*E-mail: jsgalsin@yahoo.com*

Formalism is developed, using the partial wave method in the mixed band scheme, for evaluating magnetic moments on magnetic d-band impurities in metals. The magnetic moments are calculated on d-band impurities in Ni and Pd metals and the values show reasonable agreement with the experimental results and explains the existence of giant magnetic moments in Pd alloys.

**Key Words. Electronic band structure, Metallic alloys, Magnetism.**

## INTRODUCTION

Experimental studies[1] show that even a small amount of a transition metal (TM) impurity changes drastically the electronic properties of metallic alloys. These also predict the existence of strong scattering from the TM metal impurities. Therefore, theoretical understanding of the impurity-induced changes in the various properties of transitional alloys is of immense importance from both the fundamental and technological point of views.

In magnetic alloys such as the alloys of Ni and Pd metals with 3*d*-impurities the magnetic moments are developed on the impurities, which make the impurity scattering spin dependent. The magnetic properties of these alloys depend on the electron spin polarization around the impurities. Morruzzi *et al.*[2] performed the calculations for the spin polarization of electron gas using the density functional theory. Recently the KKR (Korringa-Kohn-Rostoker) method in conjunction with the density functional approach has been employed extensively[3-5] to evaluate impurity-induced spin polarization of electron gas and magnetic moments induced on the impurities.

In this paper, an analytical formalism is developed using a simple model for an alloy in which the host metal is treated in the free electron approximation while the impurity in the simple tight binding approximation. The formalism is applied to magnetic alloys of Ni and Pd metals with 3*d*-impurities and magnetic moments on the impurities are calculated.

### Theory

In a pure metal, the wave function of conduction electrons with spin $\sigma$

is given by the Bloch wave function defined by

$$\left|\Phi^{h}_{\sigma}(\mathbf{k},\mathbf{r})\right\rangle = \left|\psi_{B\sigma}(\mathbf{k},\mathbf{r})\right\rangle = e^{ik\cdot r}\, u_{\sigma}(\mathbf{k},\mathbf{r}) \qquad (1)$$

Here k is electron wave vector and $u_{\sigma}(\mathbf{k},\mathbf{r})$ is a scalar periodic function. The conduction electron density with spin σ in a host metal is given by the square of Bloch wave function. In a substitutional alloy, the strength of conduction electron scattering from a magnetic TM impurity ion is different from that of the host metal ions. Hence, the conduction electron wave function of the host metal with a magnetic impurity $\left|\Phi^{i}_{\sigma}(\mathbf{k},\mathbf{r})\right\rangle$ will be a linear combination of the scattered Bloch wave function $\left|\psi'_{B\sigma}(\mathbf{k},\mathbf{r})\right\rangle$ of the conduction electrons and the wave function corresponding to the d-band of the impurity atom $\left|\psi^{i}_{\ell\sigma}(\mathbf{k},\mathbf{r})\right\rangle$, i.e.,

$$\left|\Phi^{i}_{\sigma}(\mathbf{k},\mathbf{r})\right\rangle = \left|\psi'_{B\sigma}(\mathbf{k},\mathbf{r})\right\rangle + \left|\psi^{i}_{\ell\sigma}(\mathbf{k},\mathbf{r})\right\rangle \qquad (2)$$

Here $\left|\psi'_{B\sigma}(\mathbf{k},\mathbf{r})\right\rangle$ and $\left|\psi^{i}_{\ell\sigma}(\mathbf{k},\mathbf{r})\right\rangle$ are evaluated in the partial wave analysis and the simple tight binding approximation as done by Gupta and Singh[6]. Therefore, the conduction electron density with spin σ in the presence of the impurity is given by $\left|\Phi^{i}_{\sigma}(\mathbf{k},\mathbf{r})\right|^2$. Hence the change in conduction electron density having spin σ can be written as

$$\Delta n_{\sigma}(\mathbf{k},\mathbf{r}) = \left|\Phi^{i}_{\sigma}(\mathbf{k},\mathbf{r})\right|^2 - \left|\Phi^{h}_{\sigma}(\mathbf{k},\mathbf{r})\right|^2 \qquad (3)$$

Substituting eqs. (1) and (3) in eq. (4) and integrating over k and simplifying we can write

$$\Delta n_{\sigma}(\mathbf{r}) = \Delta n_{f\sigma}(\mathbf{r}) + \Delta n_{\ell\sigma 1}(\mathbf{r}) + \Delta n_{\ell\sigma 2}(\mathbf{r}) \qquad (4)$$

$$\Delta n_{\ell\sigma 2}(\mathbf{r}) = \Delta n_{l\sigma 3}(\mathbf{r}) + \Delta n_{l\sigma 4}(\mathbf{r}) \qquad (5)$$

$$\Delta n_{f\sigma}(r) = \Delta n_{\ell\sigma 1}(r)$$

$$\frac{5}{4\pi^2} \frac{\sin^2\delta_{d\sigma}(k_{FH})\cos(2k_{FH}r + \delta_{d\sigma}(k_{FH}))}{r^3} \quad (6)$$

$$\Delta n_{\ell\sigma 1}(r) = \frac{(2\ell+1)k_{FH}^3}{24\pi^3}\left[R^i_{\ell\sigma}(r)\right]^2 \quad (7)$$

$$\Delta n_{d\sigma 3}(r) =$$

$$\frac{-\sqrt{5}}{2\pi^{5/2}} \frac{R^i_{d\sigma}(r)}{r^3}\left[3\,Si(k_{FH}r) + k_{FH}r\ \cos k_{FH}r - 4\sin k_{FH}r\right] \quad (8)$$

$$\Delta n_{d\sigma 4}(r) =$$

$$= \frac{5^{3/2}}{2\pi^{5/2}} \frac{R^i_{d\sigma}(r)}{r^3} \sin\delta_{d\sigma}(k_{FH})$$

$$[\,k_{FH}r\sin\{k_{FH}r + \delta_{d\sigma}(k_{FH})\} + \cos\{k_{FH}r + \delta_{d\sigma}(k_{FH})\}\,] \quad (9)$$

$$Si(k_{FH}r) = \int_0^{k_{FH}r} \frac{\sin x}{x}\,dx \quad (10)$$

Here $k_{FH}$, $\delta_{\ell\sigma}(k_{FH})$ are Fermi wave vector and phase shifts. We have retained only d-phase shift, which gives major contribution to the conduction electron density. To include the effects of m-m hybridization equal weightage is given to all the $(2\ell+1)$ sub bands. The atomic orbital in spherical coordinates is written as

$$\left|\Phi^i_{\ell m\sigma}(r)\right\rangle = R^i_{\ell\sigma}(r)\left|\ Y^m_\ell(\theta,\varphi)\right\rangle \quad (11)$$

where $R^i_{\ell\sigma}(r)$ is the radial wave function of the impurity atom and $Y^m_\ell(\theta,\varphi)$ are the spherical harmonics. The radial wave function $R^i_d(r)$ is taken from Gupta and Singh[6]. Eqs. (8) and (9) exhibit

$R_{d\sigma}(r)/r^3$ and $R_{d\sigma}(r)/r^2$ behaviour instead of the usual $1/r^3$ and $1/r^2$ behaviour.

## RESULTS AND DISCUSSION

To evaluate the different contributions to spin-dependent electron redistribution induced by impurities we need three basic parameters: $k_{FH}$, $\delta_{\ell\sigma}(k_{FH})$ and $R^i_d(r)$. The parameter $k_{FH}$ can be calculated from the valence of the host metal. $\delta_{\ell\sigma}(k_{FH})$ for the *d*-electrons can be obtained by satisfying the Friedel sum rule in terms of the total number of d-electrons $N_d$ and the number of d-electrons with spin σ, *i.e.*, $N_{d\sigma}$. Here, the formalism to Ni- and Pd-based alloys with 3*d*-impurities is applied. $N_{d\sigma}$ for Pd and Ni alloys are taken from van Acker *et al.*[7] and Zeller[4,5], respectively, and $\delta_{d\sigma}(k_{FH})$ are evaluated. Using these parameters $\Delta n_\sigma(r)$, for both spins, has been calculated for Ni and Pd alloys. The spin density distribution in an alloy is given by the difference of the electron densities of the two types of spins, *i.e.*,

$$\Delta n_{spin}(r) = \Delta n_{\uparrow}(r) - \Delta n_{\downarrow}(r) \tag{12}$$

Local magnetic moment $\mu_{loc}$ and total magnetic moment $\mu_{tot}$ on an impurity is calculated by integrating the spin density distribution over the Wigner-Seitz (WS) and over the entire volume of the crystal, respectively. We have calculated $\mu_{loc}$ and $\mu_{tot}$ for 3*d*-impurities Pd and Ni metals and the calculated values are given in Tables 1 and 2 along with other theoretical and experimental values for comparison. From Tables 1 and 2 it is evident that there is a small difference between the values of $\mu_{loc}$ and $\mu_{tot}$ as the main contribution to the magnetic moment comes from the WS sphere of the impurity and in this region d-band contribution dominates. The novel feature of the present calculation is that we have used a simple model to evaluate the magnetic moments on the impurities and it yields results comparable with the *ab initio* calculations[4,5]. Further, the present calculations explain reasonably well the giant magnetic moments observed on Fe and Co impurities in Pd alloys.

TABLE-1
CALCULATED AND EXPERIMENTAL VALUES OF LOCAL AND TOTAL MAGNETIC MOMENTS (IN TERMS OF $\mu_B$) FOR Pd ALLOYS WITH 3*d*-IMPURITIES

| Impurity | Present Results | | Other Theoretical Results | | | |
|---|---|---|---|---|---|---|
| | | | Local Moments | | Total Moments | |
| | $\mu_{loc}$ | $\mu_{tot}$ | $\mu_{loc}$ | $\mu_{exp}$ | $\mu_{tot}$ | $\mu_{exp}$ |
| Cr | 1.14 | 1.141 | 3.01[5] | --------- | 0.77[5] | ------- |
| | | | 2.950[5] | | 2.259[5] | |
| Fe | 10.41 | 10.74 | 3.439[5] | 3.5±.04[8] | 7.36[5] | 10.0[8] |
| | | | 3.383[5] | | 4.658[5] | 10.0-12.0[8] |
| Co | 9.93 | 10.53 | 2.280[5] | 2.1±0.03[8] | 7.57[5] | 9.0-10.0[8] |
| | | | 2.254[5] | | 3.955[5] | 10.8[8] |

TABLE-2
CALCULATED AND EXPERIMENTAL VALUES OF LOCAL MAGNETIC MOMENTS (IN TERMS OF $\mu_B$) FOR Ni ALLOYS WITH 3*d*-IMPURITIES

| Impurity | Present Results | Other Theoretical and Experimental Results | |
|---|---|---|---|
| | $\mu_{loc}$ | $\mu_{loc}$ | $\mu_{exp}$ |
| V | -0.59 | -0.48[4,9] | -1.15[10] |
| | | -0.56[4,9] | -0.05[10] |
| Cr | -0.24 | -1.45[4,9] | -0.15[10] |
| | | 0.2 ± 0.6[4,9] | -1.20[10] |
| Mn | 2.90 | 2.92[4,9] | 2.40[10] |
| | | 3.02[4,9] | 3.23[10] |
| Fe | 2.84 | 2.67[4,9] | 2.65[10] |
| | | 2.70[4,9] | 2.85[10] |

## ACKNOWLEDGEMENTS

The author acknowledges gratefully the financial assistance provided by CSIR, New Delhi.

## REFERENCES

1. J. Singh Galsin, Impurity Scattering in Metallic Alloys, Kluwer Acadmic and Plenum Publs, New York, p.147 (2002).
2. L. Morruzzi, J.F. Janak and A.R. Williams, Calculated Properties of Metals, Pergamon Press, London (1978).
3. P.H. Dederichs, R. Zeller, H. Akai and H. Ebert, *J Magn. Magn. Mater.*, **100**, 241 (1991).
4. R. Zeller, *J. Phys. F: Met. Phys.*, **17**, 2123 (1987).
5. R. Zeller, *Modelling Simul. Mater. Sci. Eng.*, **1**, 553 (1993).
6. D. Gupta and J. Singh, *J. Res: Punjab Agric. Univ.*, **42**, 184 (2005).
7. J.F. van Acker, W. Speier and R. Zeller, *Phys. Rev. B*, **43**, 9558 (1991).
8. C.G. Low and T.M. Holden, *Proc. Phys. Soc.*, **89**, 119 (1966); G.J. Nieuwenhuys, *Adv. Phys.*, **24**, 515 (1975); R.P. Peter, C. Buchal, K. Kubota, R.M. Mueller and F. Pobell, *Phys. Rev. Lett.*, **53**, 1108 (1984).
9. F. Kajzar and G. Parette, *J. Magn. Magn. Mater.*, **17-19**, 87 (1980).
10. J.W. Cable and R.A. Medina, *Phys. Rev.*, **B13**, 4868 (1976); R. Chakravarty and R.L. Madhav, *J. Phys. F: Met. Phys.*, **11**, 2077 (1981); F. Collins and J.B. Forsyth, *Phys. Phil. Mag.*, **8**, 401 (1963); G.G.E. Low and M.F. Collins, *J. Appl. Phys.*, **34**, 1195 (1963); C.G. Shull and M.K. Wilkinson, *Phys. Rev.*, **B97**, 304 (1955); M.F. Collins and D.A. Wheeler, *Proc. Phys. Soc.*, **82**, 633 (1963); J.W. Cable and H.R. Child, *Phys. Rev.*, **B10**, 4607 (1974); S. Blugel, H. Akai, R. Zeller and P.H. Dederichs, *Phys. Rev.*, **B35**, 3271 (1987).