weaken the interaction at a critical concentration in the range of 70–80 at.% scandium. Similar observations were made in magnetization studies on the Gd–Sc system.[6]

The most obvious difference between Sc and Y as a nonmagnetic diluent for the rare earths is the much smaller atomic volume of Sc, about 25% less than that of Y. In the simple Ruderman-Kittel-Kasuya-Yosida theory, no dependence of exchange energy on volume is predicted although there is a very slight variation of exchange energy with the c/a ratio. That volume change is an important parameter has been discussed by Wollan[7] who has compared, quantitatively, the effects of such changes with the corresponding changes brought about in the pure metals by the application of high pressures.

Three alloys in the Tb–Sc system were analyzed

quantitatively to determine the moment values in the magnetically ordered alloy. The specimens were filed to eliminate preferred orientation and annealed to relieve the stresses induced by filing. The coherent magnetic reflections were placed on an absolute scale by comparison with the scattering from a standard Ni sample. The data for two specimens with the helical structure agreed with that for the one ferromagnetic composition and with predictions based on the free-atom ordered moment of $9.0\mu_B$ for Tb, zero moment on Sc, and the Tb^{+3} ion form factor.[8]

ACKNOWLEDGMENTS

[6] H. E. Nigh, S. Legvold, F. H. Spedding, and B. J. Beaudry, J. Chem. Phys. 41, 3799 (1964).
[7] E. O. Wollan, Phys. Rev. 160, 369 (1967).

[8] See, for example, the form factor of Tb in TbIr₂, G. P. Felcher and W. C. Koehler, Phys. Rev. 131, 1518 (1963).

Electrical Resistivity and Screening in Some Dilute Ferromagnetic Nickel Alloys

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By observing departures from Matthiessen's rule, the electrical resistivity for each spin direction in dilute ferromagnetic Ni-Co and Ni-Fe alloys has been obtained. A phase-shift calculation for the majority spin carriers was performed to determine the parameters of a square-well potential assumed to represent the impurity center. From the potentials, values of the characteristic thermopower and the changes in the electronic specific heat, on alloying, for these electrons have been obtained.

I. INTRODUCTION

IT is well known that the electrical resistivity of the ferromagnetic elements exhibits a T^2 temperature dependence at low temperatures.[1–4] The explanation of this effect is not fully understood; electron-electron collisions give rise to such a temperature dependence,[5,6] as does electron-magnon scattering.[7–9] However, in

either case, the electron may change its spin direction upon collision, whereas with phonon scattering and impurity scattering (in an alloy) this is not possible. The fact that electrons can change their spin direction as the temperature increases, in a ferromagnetic alloy, leads to several interesting features in the electrical resistivity, the interpretation of which can give insight into the electronic structure of the ferromagnetic elements for the two spin directions.

In this paper, the resistivity results on three Ni-Co alloys of concentration 1.1, 2.2, and 4.7 at.% Co and two Ni-Fe alloys of concentration 1.8 and 4.6 at.% are analyzed. In these systems extremely large departures from Matthiessen's rule (MR) were observed, along with very small values[2] of $\delta\rho$, the increase in residual resistivity per atomic percent impurity. (In fact, the value of $\delta\rho$ for the Ni-Co system is smaller than that in most of the homovalent noble-metal alloys.) The band structure of Ni near the Fermi level is shown schematically in Fig. 1. The d band for the spin-$\downarrow$ electrons

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[1] G. K. White and S. B. Woods, Phil. Trans. Roy. Soc. London A251, 273 (1959).
[2] T. Farrell and D. Greig, Proc. Phys. Soc. (London) J. Phys. C (to be published).
[3] P. Radhakrishna and M. Nielsen, Phys. Status Solidi 11, 111 (1965).
[4] G. K. White and R. J. Tainsh, Phys. Rev. Letters 19, 165 (1967).
[5] W. G. Baber, Proc. Roy. Soc. (London) A158, 130 (1937).
[6] J. Appel, Phil. Mag. 8, 1071 (1963).
[7] T. Kasuya, Progr. Theoret. Phys. (Kyoto) 22, 227 (1959).
[8] I. Mannari, Progr. Theoret. Phys. (Kyoto) 22, 335 (1959).
[9] I. A. Campbell, A. Fert, and A. R. Pomeroy, Phil. Mag. 15, 977 (1967).

(majority carriers) is saturated, while approximately 0.6 holes exist in the spin-$\uparrow$ d band. In the analysis the small amount of s-electron polarization will be neglected and it will be assumed that each s-band contains 0.3 electrons. Furthermore, the effective mass of the majority carriers is taken to be $1.5m_0$ and the value of E_F is 0.59 Ry.

II. RESISTIVITY

The total resistivity of a ferromagnetic alloy at any temperature T is given by[10]

$$\rho_T = \frac{(\rho_{0\uparrow}+\rho_{p\uparrow})(\rho_{0\downarrow}+\rho_{p\downarrow})+\tfrac{1}{2}\rho_{\uparrow\downarrow}(\rho_{p\uparrow}+\rho_{p\downarrow}+\rho_{0\uparrow}+\rho_{0\downarrow})}{\rho_{0\uparrow}+\rho_{0\downarrow}+\rho_{p\uparrow}+\rho_{p\downarrow}+2\rho_{\uparrow\downarrow}},$$

(1)

where $\rho_{0\uparrow}$, $\rho_{0\downarrow}$ are the impurity resistivities and $\rho_{p\uparrow}$, $\rho_{p\downarrow}$ are the pure-material resisitivities for the two spin directions. The term $\rho_{\uparrow\downarrow}$ represents the "spin-flip" resisitivity and is related to the T^2 resisitivity. For a detailed discussion of $\rho_{\uparrow\downarrow}$, the reader is referred to Ref. 2. For an ideally pure material, $\rho_{0\uparrow}$ and $\rho_{0\downarrow}$ are zero, and hence

$$\rho_{iT} = \frac{\rho_{p\uparrow}\rho_{p\downarrow}+\tfrac{1}{2}\rho_{\uparrow\downarrow}(\rho_{p\uparrow}+\rho_{p\downarrow})}{\rho_{p\uparrow}+\rho_{p\downarrow}+2\rho_{\uparrow\downarrow}}.$$

(2)

The low-temperature residual resistivity (for two bands conducting in parallel) is given by

$$\rho_{0,\mathrm{LT}} = \rho_{0\uparrow}\rho_{0\downarrow}/(\rho_{0\uparrow}+\rho_{0\downarrow}),$$
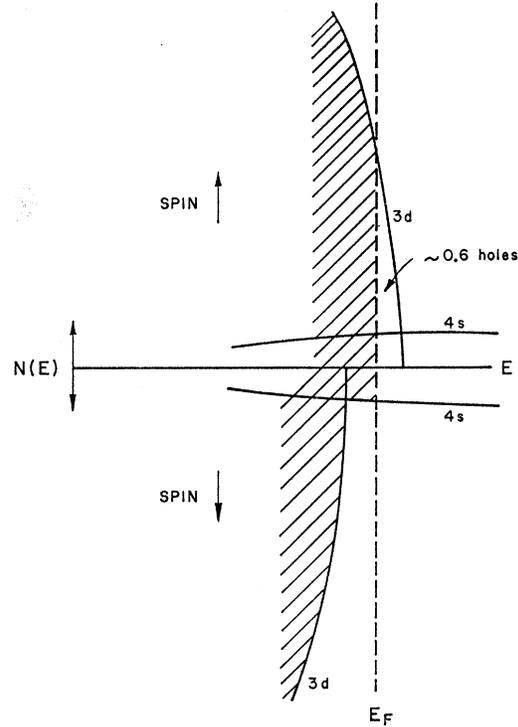
(3)

FIG. 1. Density of states in ferromagnetic nickel near the Fermi level (schematic).

and, therefore, for MR to be valid, we have

$$\rho_T' = \rho_{iT}+\rho_{0,\mathrm{LT}}$$

(4)

and the departures from MR given by

$$\Delta = \rho_T - \rho_T'$$

$$= \frac{(\rho_{0\uparrow}+\rho_{p\uparrow})(\rho_{0\downarrow}+\rho_{p\downarrow})+\tfrac{1}{2}\rho_{\uparrow\downarrow}(\rho_{0\uparrow}+\rho_{0\downarrow}+\rho_{p\uparrow}+\rho_{p\downarrow})}{\rho_{0\uparrow}+\rho_{0\downarrow}+\rho_{p\uparrow}+\rho_{p\downarrow}+2\rho_{\uparrow\downarrow}}$$

$$- \frac{\rho_{0\uparrow}\rho_{0\downarrow}(\rho_{p\uparrow}+\rho_{p\downarrow}+2\rho_{\uparrow\downarrow})+(\rho_{0\uparrow}+\rho_{0\downarrow})[\rho_{p\uparrow}\rho_{p\downarrow}+\tfrac{1}{2}\rho_{\uparrow\downarrow}(\rho_{p\uparrow}+\rho_{p\downarrow})]}{(\rho_{0\uparrow}+\rho_{0\downarrow})(\rho_{p\uparrow}+\rho_{p\downarrow}+2\rho_{\uparrow\downarrow})}$$

$$= \frac{[(\alpha-\beta)(1+\alpha)\rho_p+\alpha(1-\beta)\rho_{\uparrow\downarrow}]^2\rho_{0,\mathrm{LT}}}{\alpha(1+\beta)^2(1+\alpha)^2\rho_{0,\mathrm{LT}}\rho_p+2\alpha^2(1+\beta)^2\rho_{0,\mathrm{LT}}\rho_{\uparrow\downarrow}+\beta(1+\alpha)^4\rho_p^2+4\alpha\beta(1+\alpha)\rho_p\rho_{\uparrow\downarrow}+4\alpha^2\beta\rho_{\uparrow\downarrow}^2},$$

(5)

where $\rho_p=\rho_{p\uparrow}\rho_{p\downarrow}/(\rho_{p\uparrow}+\rho_{p\downarrow})$, $\alpha=\rho_{p\uparrow}/\rho_{p\downarrow}$, and $\beta=\rho_{0\uparrow}/\rho_{0\downarrow}$. Equation (5) is the general expression for the departures from MR in these ferromagnetic alloys. We can make the following two approximations:

(a) At low temperatures, $\rho_{0,\mathrm{LT}}$ dominates the resisitivity and $\rho_{\uparrow\downarrow}$ is the more important of the temperature-dependent terms. In this temperature region,

Eq. (5) reduces to

$$\Delta_{\mathrm{LT}} = \tfrac{1}{2}\left[\frac{(1-\beta)}{(1+\beta)}\right]^2\rho_{\uparrow\downarrow}$$

$$= \tfrac{1}{2}\left[\frac{(\rho_{0\uparrow}-\rho_{0\downarrow})}{(\rho_{0\uparrow}+\rho_{0\downarrow})}\right]^2\rho_{\uparrow\downarrow}.$$

(6)

The deviations are proportional to T^2 (since $\rho_{0\uparrow}$, $\rho_{0\downarrow}$ are temperature-independent and $\rho_{\uparrow\downarrow}$ is proportional to T^2), which is observed.

[10] A. A. Gomes and I. A. Campbell, Proc. Phys. Soc. (London) J. Phys. C1, 253 (1968).

TABLE I. The calculated values of residual resistivity and displaced charge for each spin direction. Also shown are the measured values of $\rho_{0,LT}$ and the high-temperature departures from Matthiessen's rule.

System	$\rho_{0,LT}$ ($\mu\Omega$ cm)	$\Delta_{HT}/\rho_{0,LT}$	$\delta\rho\downarrow$ ($\mu\Omega$ cm)	$\delta\rho\uparrow$ ($\mu\Omega$ cm)	$\delta Z\downarrow$	$\delta Z\uparrow$
	0.153	2.8				
Ni-Co	0.297	2.7	0.15	2.00	+0.1	−1.1
	0.647	2.6				
Ni-Fe	0.713	1.4	0.45	3.26	+0.1	−2.1
	1.80	1.0				

(b) At high temperatures, $\rho_{0,LT}$ is small compared with the temperature-dependent terms (provided that the alloy is sufficiently dilute), and if we assume that $\rho_{\uparrow\downarrow}$ is again the dominant term, we find

$$\Delta_{HT}=\tfrac{1}{4}[(1-\beta)^2/\beta]\rho_{0,LT} \qquad (7a)$$

or

$$\Delta_{HT}/\rho_{0,LT}=\tfrac{1}{4}[(\rho_{0\uparrow}-\rho_{0\downarrow})^2/\rho_{0\uparrow}\rho_{0\downarrow}]. \qquad (7b)$$

Thus the departures saturate at high temperatures; they are positive and their magnitude depends on the relative magnitudes of $\rho_{0\uparrow}$ and $\rho_{0\downarrow}$. For a given alloy series, the departures are characterized by the constant value of $\Delta_{HT}/\rho_{0,LT}$. The experimental values of $\Delta_{HT}/\rho_{0,LT}$ at 273°K are given in Table I, along with the values of $\rho_{0,LT}$. Since $\rho_{0,LT}=\beta/(1+\beta)$, values of $\rho_{0\uparrow}$ and $\rho_{0\downarrow}$ can be estimated for the alloys and hence values of $\delta\rho_{\uparrow}$ and $\delta\rho_{\downarrow}$ (the increase in the residual resistivity per atomic percent impurity). It must be mentioned that there are two possible solutions for β which differ by the interchange of $\rho_{0\uparrow}$ and $\rho_{0\downarrow}$. The physical solution is that where $\rho_{0\uparrow}$ is the smaller, since the presence of holes in the spin-↑ d band enhances the resistivity of the spin-↑ electrons due to impurity-induced $s\rightarrow d$ transitions. Values of $\delta\rho_{\uparrow}$ and $\delta\rho_{\downarrow}$ are given in Table I. It is interesting to note that the departures may be regarded as arising from a "temperature-dependent" residual resistivity which saturates at high temperatures to $\rho_{0,HT}$. Thus

$$\Delta=\rho_{0,HT}-\rho_{0,LT},$$

and hence

$$\rho_{0,HT}=\tfrac{1}{4}[(1-\beta)^2/\beta]\rho_{0,LT}+\rho_{0,LT}$$
$$=\tfrac{1}{4}[(1+\beta)^2/\beta]\rho_{0,LT}=\tfrac{1}{4}(\rho_{0\uparrow}+\rho_{0\downarrow}). \qquad (8)$$

The above expression for $\rho_{0,HT}$ differs from that given in Refs. 9 and 10. The authors[9,10] argue that because of spin mixing, an electron has equal probability of being spin-↑ or spin-↓, and therefore its effective high-temperature residual resistivity is $\tfrac{1}{2}(\rho_{0\uparrow}+\rho_{0\downarrow})$. However, if $\rho_{0\uparrow}=\rho_{0\downarrow}$, then $\rho_{0,HT}=\rho_{0\uparrow}$, while $\rho_{0,LT}=\tfrac{1}{2}\rho_{0\uparrow}$, i.e., a departure from MR arising when the spin-mixing mechanism is ineffective. Furthermore, $\rho_{0,HT}=\tfrac{1}{2}(\rho_{0\uparrow}+\rho_{0\downarrow})$ leads to a minimum value of $\Delta_{HT}/\rho_{0,LT}$ equal to unity, in contrast to experiment.

III. SCREENING

The displaced charge for the two spin directions is given by[11]

$$\delta Z_{\uparrow}=\tfrac{1}{2}(\Delta Z-d\bar{\mu}/dc) \qquad (9a)$$

and

$$\delta Z_{\downarrow}=\tfrac{1}{2}(\Delta Z+d\bar{\mu}/dc), \qquad (9b)$$

where ΔZ is the difference in atomic numbers between host and impurity and $d\bar{\mu}/dc$ is the rate of change of the mean magnetic moment per atomic percent impurity.

Values of $\delta Z_{\uparrow}$ and $\delta Z_{\downarrow}$ for the Ni-Co and Ni-Fe series are given in Table I. They are estimated using the values of $d\bar{\mu}/dc$ given in Ref. 13 and taking ΔZ to be −1 and −2, respectively, for the two series.

If the impurity is represented by a square-well potential, the radius and depth of the well (for the majority carriers) can be determined by solving the following two equations[12]:

$$\delta Z_{\downarrow}=1/\pi \sum_{l} (2l+1)\eta_l(E_F), \qquad (10a)$$

and

$$\delta\rho_{\downarrow}=\frac{4\pi m^* V_F}{10^2 n_{\downarrow}e^2 K_F^2} \sum_{l} (l+1)\sin^2(\eta_l-\eta_{l+1})_{E_F}, \qquad (10b)$$

where $\eta_l(E_F)$ is the phase shift for the partial wave of angular momentum quantum numbers l, and $n_{\downarrow}$ is the number of majority spin carriers.

Equation (10a) is simply a statement of the Friedel sum rule for one spin direction. From Table I it is noted that $\delta Z_{\downarrow}$ is very small for these systems, and, therefore, for consistency between Eqs. (10a) and (10b), $\delta\rho_{\downarrow}$ must also be small. These majority carriers "short circuit" the spin-↑ electrons and hence the low residual resistivity for the two systems. In other words, the low values of $\delta\rho$ for the Ni-Co and Ni-Fe series are consistent with the magnetization results.

The radius and depth of the well obtained by solving the two equations (10a) and (10b) are given in Table II. Note that the radius, effectively the screen length, is of the same order of magnitude as that in many Cu

[11] J. Kanamori, J. Appl. Phys. **36**, 929 (1965).
[12] C. M. Hurd and E. M. Gordon, J. Phys. Chem. Solids (to be published).

TABLE II. Parameters of the square-well potential, the characteristic thermopower, and changes in the density of states and electronic specific-heat coefficient on alloying.

System	Radius of well (Å)	Depth of well (eV)	$\delta N_\downarrow (E_F)$ (states/Ry atom)	$\delta S_\downarrow/T$ (μV deg^{-2})	$\delta\gamma_\downarrow$ (mJ mole^{-1} deg^{-2})
Ni-Co	1.03	0.118	$+0.078$	-4.2×10^{-3}	$+1.35\times10^{-2}$
Ni-Fe	0.67	0.214	$+0.066$	-1.7×10^{-3}	$+1.15\times10^{-2}$
					$-1.0\ \times10^{-1}$ [a]

[a] Experimental value taken from Ref. 25.

alloys,[12,13] in contrast to the over-all screening in transition metals occurring within the impurity site itself.[14] This is consistent with the recent band calculations[15-19] and Fermi-surface determinations[20-24] which suggest that the electronic structure for majority spin carriers in ferromagnetic nickel is very similar to that of copper, and also with the argument that the spin- ↑ (minority-spin) electrons do the screening in Ni^{11}.

IV. DENSITY OF STATES AND ELECTRONIC SPECIFIC HEAT

The change in the density of states at the Fermi level per single impurity atom, $\delta N(E_F)$, was estimated for the spin- ↓ electrons using

$$\delta N_\downarrow(E_F) = \frac{1}{\pi} \sum_{l=0}^{l\max} (2l+1) \left(\frac{d\eta_l}{dE}\right)_{E_F}. \qquad (11)$$

The results are given in Table II. The orders of magnitude of the $\delta N_\downarrow(E_F)$ for the two systems seem reasonable, since the density of states for the majority spin carriers in pure Ni is 4.5 (states/atom)/Ry.[19]

The change in the electronic specific heat of the host produced by the addition of one impurity atom is simply $\delta\gamma = Q\delta N(E_F)$, where $Q = \frac{1}{3}(\pi^2 K^2)$. Thus the change $\delta\gamma_\downarrow$ per unit concentration for the majority-spin electron is

$$\delta\gamma_\downarrow = QN_0\delta N_\downarrow(E_F), \qquad (12)$$

where N_0 is Avogadro's number. Values of $\delta\gamma_\downarrow$ estimated from Eq. (12) are given in Table II. Also given in Table II is the experimental value of $\delta\gamma$ for a Ni+1 at.% Fe.[25] (No data exist for very dilute Ni-Co alloys.) Note that the calculated value of $\delta\gamma$ is much smaller than the experimental value of $\delta\gamma$ and is of opposite sign. This suggests that the experimentally observed change in γ is due almost entirely to the spin- ↑ electrons. Furthermore, because of its smallness, the change in $\gamma_\downarrow$ will not affect the $d_\uparrow$-band shape derived from low-temperature specific-heat measurements on the basis of the rigid-band model.[26]

V. CHARACTERISTIC THERMOPOWER

For elastic scattering, the diffusion thermopower can be expressed as

$$S = -(QT/e)(d \ln\rho/dE)_{E_F}, \qquad (13)$$

where $Q = \frac{1}{3}(\pi^2 k^2)$ and the derivative is taken at the Fermi level. In an alloy, when the same scattering conditions prevail, a characteristic thermopower for spin- ↓ electrons $\delta S_\downarrow$ can be defined which is related to $\delta\rho_\downarrow$ according to

$$\delta S_\downarrow = -(QT/e)(d \ln\delta\rho_\downarrow/dE)_{E_F}. \qquad (14)$$

Substituting for $\delta\rho_\downarrow$ from Eq. (10b), the above expression for $\delta S_\downarrow$ becomes

$$\delta S_\downarrow = -\frac{QT}{e}\left[-\frac{1}{2E} + \sum_{l=0}^{l\max} l\sin^2(\eta_{l-1}-\eta_l)\left(\frac{d\eta_{l-1}}{dE} - \frac{d\eta_l}{dE}\right)\Big/ \sum_{l=0}^{l\max} l\sin^2(\eta_{l-1}-\eta_l)\right]_{E_F}. \qquad (15)$$

The temperature-independent quantity $\delta S_\downarrow/T$ was calculated using the above scattering potentials for Co and Fe in Ni. Values of $\delta S_\downarrow/T$ for the two systems are

given in Table II, and it is noted that they are extremely small. Unfortunately, experimental values of this quantity are unavailable, since the measured thermopower contains contributions from both spin directions. However, in view of the smallness of $\delta S_\downarrow/T$, for these systems, any significant changes in the experimental values of S/T must surely arise from changes in the thermopowers of the spin- ↑ electrons. It is conjectured here that if such changes exist (and the results[27] indicates that this is so), then they are due to the impurity-induced $s\rightarrow d$ transitions in the same way as changes in S/T arise in some Pt and Pd alloys.[28]

[13] F. J. Blatt, Phys. Rev. 108, 285 (1957).
[14] J. Friedel, Nuovo Cimento Suppl. 2, 287 (1958).
[15] J. G. Hanus, MIT Solid State and Molecular Theory Group Quarterly Progress Report No. 44, p. 29 (unpublished).
[16] S. Wakoh and J. Yamashita, J. Phys. Soc. Japan 19, 1342 (1964).
[17] S. Wakoh, J. Phys. Soc. Japan 20, 1894 (1965).
[18] J. W. D. Connolly, Phys. Rev. 159, 415 (1967).
[19] L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. 152, 505 (1966).
[20] E. Fawcett and W. A. Reed, Phys. Rev. Letters 9, 336 (1962).
[21] A. S. Joseph and A. C. Thorsen, Phys. Rev. Letters 11, 554 (1963).
[22] D. C. Tsui and R. W. Stark, Phys. Rev. Letters 17, 871 (1966).
[23] D. C. Tsui, Phys. Rev. 164, 669 (1967).
[24] H. Ehrenreich, D. Phillip, and D. J. Olechna, Phys. Rev. 131, 2469 (1963).

[25] R. Ehrat and D. Rivier, Helv. Phys. Acta 38, 643 (1965).
[26] M. Shimizu, T. Takahashi, and A. Katsuki, J. Phys. Soc. Japan 18, 801 (1963).
[27] T. Farrell and D. Greig (to be published).
[28] R. Fletcher and D. Greig, Phil. Mag. 17, 21 (1968).

VI. CONCLUSION AND SUMMARY

The low values of $\delta\rho_\downarrow$ for Ni-Co and Ni-Fe alloy series are explained and shown to be consistent with the magnetization results. These electrons (spin-$\downarrow$) "short circuit" the spin-$\uparrow$ electrons (since, in the latter case, impurity-induced $s\rightarrow d$ transitions result in a high $\delta\rho_\uparrow$) to give a low value of $\delta\rho$. The large departures from MR in these systems are accounted for on the "spin-mixing" model and are essentially due to the large difference between $\delta\rho_\uparrow$ and $\delta\rho_\downarrow$. From the parameters of a square-well potential, which was assumed to represent the impurity, the characteristic thermopower and changes in the electronic specific-heat coefficient γ were determined for the two alloy systems. In each case, the experimental values were extremely small, and it was suggested that any significant changes in γ and in the diffusion thermopower are due to the presence of the high density-of-states d band at the Fermi level, for spin-$\uparrow$ electrons.

APPENDIX

Values of the phase shifts η_l and their derivatives at the Fermi level $d\eta_l/dE_F$ calculated for the Ni-Co and Ni-Fe series are presented below. The phase shifts η_l are expressed in rad and the derivatives are given in rad/a.u. (energy).

System	η_0	η_1	η_2	η_3	η_4
Ni-Co	0.15547	0.04454	0.00463	0.00026	0.00001
Ni-Fe	0.23846	0.02359	0.00095	0.00002	0.00000

System	$d\eta_0/dE_F$	$d\eta_1/dE_F$	$d\eta_2/dE_F$	$d\eta_3/dE_F$	$d\eta_4/dE_F$
Ni-Co	−0.14725	0.14945	0.03339	0.00283	0.00013
Ni-Fe	0.06311	0.10431	0.00759	0.00025	0.00000

Tunneling in Ferroelectrics

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The Hamiltonian of a particle oscillating in a double-minimum potential well is investigated by means of the retarded Green functions of the system. The coefficients of Devonshire's free-energy function are derived.

FOLLOWING a suggestion by de Gennes,[1] we use pseudospin variables to describe protons in a set of double-minimum potential wells. The Hamiltonian is derived by the procedures outlined in Tokunaga and Matsubara[2]—we have explicitly included fourth-order terms in order to describe the four protons surrounding a PO_4 group in potassium dihydrogen phosphate (KDP).

We use the following Hamiltonian:

$$H_0 = -\Gamma\sum_1 X_1 - \sum_{12} J_{12} Z_1 Z_2 - \sum_{1234} L_{1234} Z_1 Z_2 Z_3 Z_4, \quad (1)$$

where we have neglected terms involving integrals of products of wave functions localized on different sites and at different equilibrium positions, i.e., terms of the form $\sum B_{12} X_1 Z_2$, etc., have been neglected for the latter reason.[2] Terms of the form

$$-\sum_{123} C_{123} Z_1 Z_2 Z_3$$

are also zero from symmetry reasons for temperatures above a Curie temperature T_c (to be defined later)—in the unperturbed paraelectric crystal they must give a zero contribution to the energy of the system.

We limit the discussion to temperatures $T > T_c$ and to the interaction between H_0 and a perturbation of

[1] P. de Gennes, Solid State Commun. **1**, 132 (1963).
[2] M. Tokunaga and T. Matsubara, Progr. Theoret. Phys. (Kyoto) **35**, 581 (1966).