Magnetostriction in Nickel Alloys*

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It is shown that the existence of an orbital degeneracy in the 3*d* band may lead to a change of sign of the magnetostriction, when this degeneracy goes through the Fermi level. Such a change of sign is observed in the Fe-Ni and Co-Ni alloy series (permalloy), at an electron concentration of 27.7 electrons per atom. As was shown in a previous publication, the same orbital degeneracy is probably responsible for the strong maximum of the magnetoresistance, and for the change of sign of the extraordinary Hall effect, observed in these alloys at the same value of the electron concentration.

INTRODUCTION

As was first noted by Smit,[1] the "ferromagnetic anisotropy of resistivity" $\Delta\rho/\rho_0$ (often called magnetoresistance effect) has a large maximum (Fig. 1) in Fe-Ni and Co-Ni alloys, for the same value (27.7 electrons/atom) of the electron concentration at which the extraordinary Hall effect changes sign (Fig. 2).

These singularities of the transport properties have been explained in a previous publication[2] by postulating the existence of an orbital degeneracy R close to the Fermi level of the alloy (Fig. 3). The degenerate level R, located at the intersection of two branches a and b, is split by spin-orbit interaction into two levels P and Q separated by a gap $\epsilon_P-\epsilon_Q$:

$$\epsilon_P-\epsilon_Q\lesssim 2A\hbar^2\approx 0.15\text{ eV}, \tag{1}$$

where A is the one-electron spin-orbit parameter for nickel. The spin-orbit Hamiltonian H_{so} is a periodic operator in the crystal. Using the tight-binding approximation, its matrix elements between two Bloch states may be written[3,4]:

$$\langle\psi_{k\tau}|H_{so}|\psi_{k'\tau'}\rangle\approx\delta(\mathbf{k}-\mathbf{k}')\langle\varphi_\tau|A\mathbf{L}\cdot\mathbf{S}|\varphi_{\tau'}\rangle, \tag{2}$$

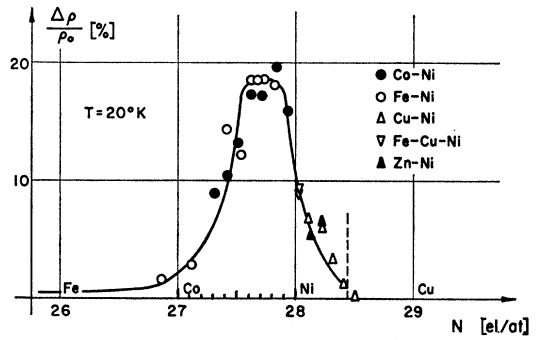

FIG. 1. The ferromagnetic anisotropy of resistivity $\Delta\rho/\rho_0=(\rho_{11}-\rho_1)/\rho_0$ in polycrystalline fcc nickel alloys at low temperature.

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[1] J. Smit, Physica **17**, 612 (1951).

[2] L. Berger, Physica, **30**, 1141 (1964); see also, Bull. Am. Phys. Soc. **6**, 447 (1961).

[3] H. Brooks, Phys. Rev. **58**, 909 (1940).

[4] G. C. Fletcher, Proc. Phys. Soc. (London) **67**, 505 (1954); see, however, *ibid.* **78**, 145 (1961).

where τ numbers the various branches of the 3*d* and 4*s* band, and where φ_τ and $\varphi_{\tau'}$ are appropriate 3*d* atomic orbitals. If we choose the z axis to be parallel to the saturation magnetization, it is the AL_zS_z part of Eq. (2) which splits the degeneracy at R, while the terms $A(L_xS_x+L_yS_y)$ play minor roles. The orbital angular momentum $\langle\mathbf{L}\rangle$ of state P is completely unquenched[2] and parallel to the spin $\mathbf{S}$ of the electron, while that of state Q is antiparallel to the spin.

The AL_zS_z perturbation of Eq. (2) strongly mixes the Bloch waves ψ_{ka} and ψ_{kb} belonging to intersecting branches a and b (Fig. 3), and corresponding to the same value of k. The Bloch waves for state P and Q are given[2] by:

$$\begin{aligned}\psi_{kP}&=(1/\sqrt{2})(\psi_{ka}+i\psi_{kb}),\\ \psi_{kQ}&=(1/\sqrt{2})(\psi_{ka}-i\psi_{kb}).\end{aligned} \tag{3}$$

The purpose of the present publication is to show that the value of the magnetostriction should change sign when such an orbital degeneracy goes through the Fermi level, in an alloy series. A change of sign of the magnetostriction occurs, in fact, in the Co-Ni and Fe-Ni alloy series (permalloy), precisely at the value of the electron concentration for which the singularities of the transport properties mentioned above have already suggested[2] the presence of an orbital degeneracy.

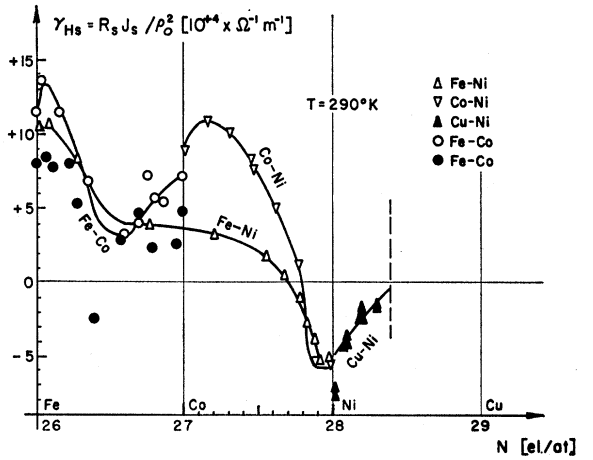

FIG. 2. The extraordinary Hall conductivity $\gamma_{HS}=R_SJ_S/\rho_0^2$ in polycrystalline fcc nickel alloys at room temperature.

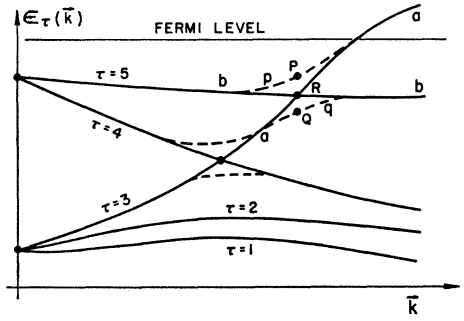

FIG. 3. Schematic representation of the 3*d* band in a fcc crystal, for spin-down electrons.

INFLUENCE OF THE DEGENERACY ON THE TRANSPORT PROPERTIES

Owing to the spin-orbit perturbation, each of the two Bloch states of Eq. (3) has a strong left-right asymmetry[2] with respect to the plane determined by **k** and the spin **S**. For example, one manifestation of the asymmetry is the existence, in each lattice cell, of an electric dipole moment perpendicular to both **k** and **S**.

As remarked by Smit,[5] in the final analysis such left-right asymmetries in the Bloch states of electrons located at the Fermi level are the cause of the extraordinary Hall effect in ferromagnets. It is easy to see[2] that the left-right asymmetry of state P is equal, but of the opposite sign, to that of state Q. We expect therefore a reversal of sign of the "extraordinary Hall conductivity" γ_{HS} when the Fermi level is shifted from state Q to state P. This is predicted[2] as well with the Karplus and Luttinger theory of γ_{HS} as with the Smit theory. In this way is explained[2] the change of sign of γ_{HS} in the Co-Ni and Fe-Ni fcc series (Fig. 2).

At the same time, it is easy to see that the transition probability for a conduction electron to be scattered into state P and Q by a spherical impurity potential depends strongly on the angle between **S** and the velocity of the incident conduction electron. This is due to the strongly distorted shape of the wave functions of Eq. (3). A large value of the "ferromagnetic anisotropy of resistivity" $\Delta\rho/\rho_0=(\rho_{11}-\rho_\perp)/\rho_0$ results therefore[2] when the Fermi level of the alloy is close to states P and Q, in agreement with the experimental data for fcc Co-Ni and Fe-Ni alloys at low temperature (Fig. 1). In the definition of this anisotropy, ρ_{11} and $\rho_\perp$ are the resistivities measured in directions respectively parallel and perpendicular to the saturation magnetization, and ρ_0 is the zero-field resistivity.

The large value $\Delta\rho/\rho_0=20\%$ is the most direct evidence for the existence of a degeneracy. In general $\Delta\rho/\rho_0$ is expected to be of the order of $(A\hbar^2/\Delta\epsilon)^2$, where $\Delta\epsilon$ is some average energy difference between branches. Usually, this would give only 1%, in agreement with the experimental value of $\Delta\rho/\rho_0$ in many materials. In order to obtain 20%, two branches must come unusually close together.

NATURE OF THE DEGENERACY

One should realize that it is not really necessary to have an exact degeneracy R. If two branches come close together, at a distance of the order of $2A\hbar^2=0.15$ eV or less, all that has been said here will apply without important modification. Branches a and b will still be strongly mixed together by the spin-orbit perturbation.

This quasidegeneracy is likely to be most complete in the neighborhood of symmetry axes or symmetry planes of k space.[6] The problem then arises of understanding how such small regions of k space can play any considerable role in the transport phenomena or in the magnetostriction. A possible answer may be the following. It is well known that the point where a symmetry axis meets the zone boundary or the origin of k space corresponds either to the edge of a subband, or to a "critical point"[7] of the band structure. The region of k space close to such a critical point contributes a considerable part of the density of states. Our orbital degeneracy (or quasidegeneracy) R may well be located close to the zone boundary or to the origin, and one (or both) of the two branches constituting the degeneracy may be associated with a critical point in the band structure of Fe-Ni and Co-Ni alloys.

An optical transition with a photon energy of 0.3 eV has recently been observed in pure nickel. It seems to be associated[8–10] with certain critical points located at

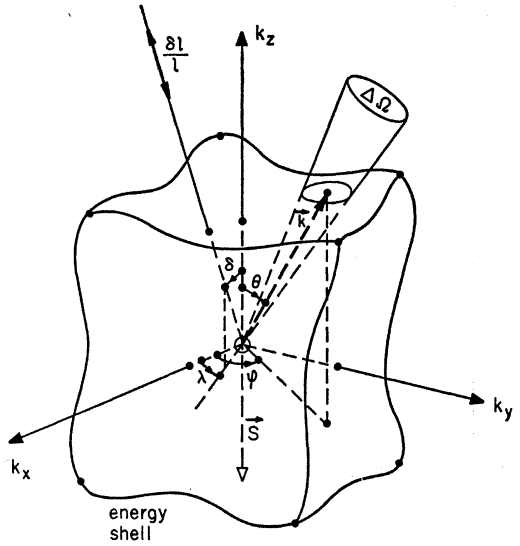

FIG. 4. Energy shell in k space, at the energy ϵ. The energy shell is divided into finite regions, corresponding each to a solid angle $\Delta\Omega$.

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[7] L. Van Hove, Phys. Rev. **89**, 1189 (1953).

[8] H. Ehrenreich, H. R. Philipp, and D. J. Olechna, Phys. Rev. **131**, 2469 (1963).

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point L where the 111 axis meets the zone boundary, in the band of spin-up electrons. These critical points are close to the Fermi level of nickel ($N=28$). Assuming[11] a density of states of 2 electrons/eV/atom, the Fermi level of our Fe-Ni and Co-Ni alloys ($N=27.7$) differs from that of nickel by only 0.15 eV in the case of spin-down electrons, and probably still less in the case of spin-up electrons. Optical transitions happen mostly between states of different parity, and spin-orbit interaction has zero matrix elements between such states; it is therefore unlikely that the two critical points associated with this transition are both involved in our quasidegeneracy. But at least one of them might be involved. However, as the critical points located at point X, on the 100 axis, are a possibility too, we will leave the detailed discussion of the location of the degeneracy to another paper.

MAGNETOSTRICTION IN THE PRESENCE OF AN ORBITAL DEGENERACY

The band theory of magnetostriction has been developed by a few authors.[12,13] Like $\Delta\rho/\rho_0$ and γ_{HS}, the magnetostriction of ferromagnets is due mainly to spin-orbit interaction [Eq. (2)].

The total energy E_0 of the $3d$ electrons at zero temperature may be written in the absence of spin-orbit interaction, and in the absence of any strain:

$$E_0=\int_0^{\epsilon_F{}^0}\epsilon\nu_0(\epsilon)d\epsilon. \tag{4}$$

For any small change of the band structure, we can compute the new energy E. If the new density of states is $\nu=\nu_0+\delta\nu$, we have

$$E=\int_0^{\epsilon_F{}^0}\epsilon(\nu_0(\epsilon)+\delta\nu(\epsilon))d\epsilon+\delta\epsilon_F\epsilon_F{}^0\nu(\epsilon_F{}^0)\,, \tag{5}$$

where $\epsilon_F{}^0+\delta\epsilon_F$ is the new Fermi level.

The total number of electrons remains constant:

$$\int_0^{\epsilon_F{}^0}\delta\nu(\epsilon)d\epsilon+\delta\epsilon_F\nu_0(\epsilon_F{}^0)=0. \tag{6}$$

Combining Eqs. (5) and (6), we obtain

$$E=E_0+\int_0^{\epsilon_F{}^0}(\epsilon-\epsilon_F{}^0)\delta\nu(\epsilon)d\epsilon. \tag{7}$$

We assume that the changes in the band structure are due to the introduction of spin-orbit interaction [Eq. (2)], and also to the application of a uniaxial strain $\delta l/l$. When computing $\delta\nu(\epsilon)$, we must be careful to keep the terms proportional to the product of the strain and of powers of the spin-orbit parameter A, as these terms are the ones giving rise to the magnetoelastic energy.

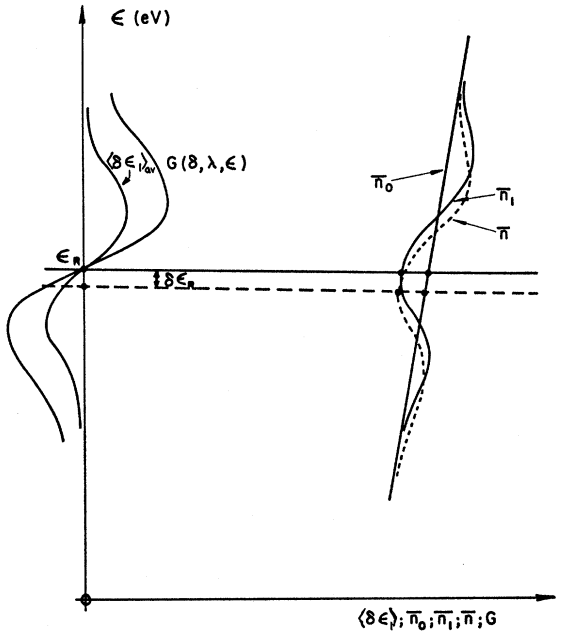

FIG. 5. Behavior of the spin-orbit shift $\langle\delta\epsilon_1\rangle_{av}$, of the local densities of states $\bar{n}_0$, $\bar{n}_1$, and $\bar{n}$, and of the magnetostriction G, as a function of energy.

Let us introduce the local density of states $\bar{n}_0(\theta,\varphi,\epsilon)$, averaged over a finite solid angle $\Delta\Omega$ around a direction (θ,φ) of k space (Fig. 4):

$$\begin{aligned}\bar{n}_0(\theta,\varphi,\epsilon)&=\Delta N/\Delta\Omega d\epsilon\,,\\ \nu_0(\epsilon)&\approx\int\bar{n}_0(\theta,\varphi,\epsilon)d\Omega\,,\end{aligned} \tag{8}$$

where the integral extends over all directions of k space, on the $3d$ energy shell at energy ϵ.

First, we switch on spin-orbit interaction alone [Eq. (2)]. The individual $3d$ states, located in the solid angle $\Delta\Omega$, are displaced on the average by $\langle\delta\epsilon_1(\theta,\varphi,\epsilon)\rangle_{av}$ on the energy scale. The shift is different on the various parts of an energy shell. If $\langle\delta\epsilon_1\rangle_{av}$ is small, the conservation of the number of states gives

$$\bar{n}_1(\theta,\varphi,\epsilon)\approx\bar{n}_0-\frac{\partial}{\partial\epsilon}(\bar{n}_0\langle\delta\epsilon_1\rangle_{av})\,, \tag{9}$$

where $\bar{n}_1$ is the new local density of states.

If an orbital degeneracy R, split by spin-orbit interaction, is present (Fig. 3), the shift $\delta\epsilon_1$ is positive above R, and negative below R (Fig. 5). This expresses the "repulsion" between state P and state Q, caused by spin-orbit interaction.

In principle, the shift may reach a value $\pm A\hbar^2\approx\pm0.075$ eV. However, as the $3d$ band structure is not

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[13] G. C. Fletcher, Proc. Phys. Soc. (London) **A68**, 1066 (1955).

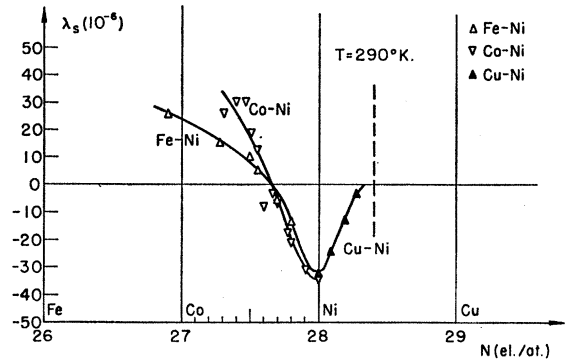

FIG. 6. The saturation magnetostriction λ_S in polycrystalline fcc nickel alloys at room temperature, plotted against the electron concentration N.

spherical, the degeneracy R corresponds to different energies in the various directions of k space.[2] Therefore the degeneracy does not pass at the Fermi level simultaneously on every point of the Fermi surface. As the quantities represented in Fig. 5 are obtained by averaging over the finite solid angle $\Delta\Omega$ on an energy shell, a spreading out of the curves will take place on the energy scale. For example, the extrema of the average shift $\langle\delta\epsilon_1\rangle_{av}$ will be located further away from the energy ϵ_R, and the extremum value will be correspondingly reduced. An identical broadening and decrease happens in the case of the extraordinary Hall conductivity (see Fig. 6 of Ref. 2).

Because of this smearing effect, there is no "gap" in the density of states $\bar{n}_1$ at the energy ϵ_R, but only a small decrease of its value (Fig. 5).

Secondly, we apply a uniaxial strain $\delta l/l$, in a direction (δ,λ) of space (Fig. 4), keeping the volume constant. Its effect is to shift the energy of the degeneracy R, located in the direction (θ,φ), by an amount

$$\delta\epsilon_R = V(\delta,\lambda,\theta,\varphi)(\delta l/l)\,, \tag{10}$$

where V has the dimension of an energy. The value of V is probably of the order of the electron volt and its sign is unknown *a priori*. The entire resonance curve for $\bar{n}_1$ is shifted accordingly (Fig. 5). The local density of states becomes finally

$$\bar{n}\approx\bar{n}_1-\delta\epsilon_R(\partial\bar{n}_1/\partial\epsilon)\,. \tag{11}$$

We have for ν an equation similar to Eq. (8):

$$\nu(\epsilon)\approx\int\bar{n}(\theta,\varphi,\epsilon)d\Omega. \tag{12}$$

Combining Eqs. (7) to (12) together, and remembering that $\nu=\nu_0+\delta\nu$, we obtain

$$E=E_0+\frac{\delta l}{l}\int_0^{\epsilon_F{}^0}(\epsilon-\epsilon_F{}^0)\frac{\partial^2 G}{\partial\epsilon^2}d\epsilon\,, \tag{13}$$

where

$$G(\delta,\lambda,\epsilon)=\int V\bar{n}_0\langle\delta\epsilon_1\rangle_{av}d\Omega\,, \tag{14}$$

and where only the terms which contain the product of the strain and of $\langle\delta\epsilon_1\rangle_{av}$ are kept.

Integrating by parts, we get finally

$$E-E_0=-(\delta l/l)G(\delta,\lambda,\epsilon_F{}^0)\,. \tag{15}$$

This is the magnetoelastic energy. The coefficient G is a measure of the magnetostriction. We see that the magnetoelastic energy (or the magnetostriction) depends only on the electrons located at the Fermi level of the alloy. It is directly proportional to the spin-orbit energy shifts $\langle\delta\epsilon_1\rangle_{av}$ at the Fermi level.

As mentioned before, the spin-orbit shifts are positive above the degeneracy R (branch p), and negative below (branch q). Therefore, according to Eq. (14), the magnetostriction $G(\delta,\lambda,\epsilon_F{}^0)$ should change sign when the Fermi level $\epsilon_F{}^0$ goes through the degeneracy (Fig. 5). This is what we wanted to prove.

COMPARISON WITH EXPERIMENTAL DATA

The saturation magnetostriction λ_s has been measured by several authors in polycrystalline fcc Fe-Ni alloys,[14,15] Ni-Cu alloys,[15,16] Co-Ni alloys.[15,16] Some of the values at room temperature have been plotted as a function of the electron concentration N in Fig. 6. The curves for zero temperature would not be very different.[15] The quantity λ_s represents a spontaneous strain in the polycrystal along Oz, obtained by minimizing the sum of the magnetoelastic energy [Eq. (15)] and of the elastic energy $\frac{1}{2}vY(\delta l/l)^2$. It is proportional to our quantity G:

$$\lambda_s=G(0,0,\epsilon_F{}^0)/Yv\,, \tag{16}$$

where Y is Young's modulus, and v the volume of the crystal.

The rigid band model is expected to be valid for these alloys,[17] as the difference in atomic number of the components is not larger than two.

The magnetostriction λ_s changes sign (Fig. 6) at an electron concentration $N=27.65$ e/atom. This is practically identical to the value $N=27.7$ for which the "ferromagnetic anisotropy of resistivity" $\Delta\rho/\rho_0$ has a large maximum of 20% at low temperature (Fig. 1), and for which the extraordinary Hall effect changes sign (Fig. 2).

The effect of an orbital degeneracy on the magnetostriction of ferromagnetic alloys is very similar to the effect of a zone boundary (and of the corresponding band gap) on the ratio c/a for the hcp lattice of magnesium alloys.[18] It should however be remarked that because of broadening effects, the orbital degeneracy

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[15] J. J. Went, Physica **17**, 99 (1951).
[16] M. Yamamoto and T. Nakamichi, Sci. Rept. Res. Inst. Tohoku Univ. **A11**, 168 (1959).
[17] J. Friedel, Nuovo Cimento, Suppl. **7**, 287 (1958).
[18] J. B. Goodenough, Phys. Rev. **89**, 282 (1953). See Figs. 9 and 10 of this paper.

causes no real gap, but only a small decrease of the density of states.

In the case of pure nickel, the measurements give (Fig. 6): $\lambda_s=-35\times10^{-6}$. Taking $Y=2\times10^{11}$ N/m^2, $v=4.35\times10^{-29}$ m^3/atom, $\nu_0(\epsilon_F{}^0)=2$ e/eV /atom, and assuming $V\approx0.5$ eV, this gives roughly, by Eqs. (16) and (14):

$$\langle\delta\epsilon_1(\epsilon_F{}^0)\rangle_{\rm av}\approx\frac{\lambda_s Y v}{V\nu_0(\epsilon_F{}^0)}\approx2\times10^{-3}\text{ eV}. \qquad (17)$$

This is 35 times smaller than the maximum possible value $A\hbar^2$. As explained before, the nonsphericity of the Fermi surface is indeed expected to lower the average spin-orbit shifts, on each side of the place where they change sign. However, Eq. (17) gives only an order of magnitude, at best, as the integral of Eq. (14) has been replaced by a product, and V assumed constant on a whole energy shell. The variation of V on the various parts of an energy shell plays, in fact, an essential role in the phenomenon of magnetostriction.

LIMITATIONS OF THE THEORY, AND CASE OF OTHER NICKEL ALLOYS

The present theory takes into account only the mutual perturbation of the two branches a and b which cross at the degeneracy R. This is permissible only if the other $3d$ and $4s$ branches are sufficiently far above or below R that their effect be negligible. For the same reason, the theory applies only to the range of alloys where R is close to the Fermi level. Finally, the quasi-degeneracy must affect a considerable part of the $3d$ states present at the Fermi level. As explained before, this is possible if the Fermi level is close to a critical point of the band structure.

Moreover, we take into account only the AL_zS_z part of $A\mathbf{L}\cdot\mathbf{S}$. The rest is not affected by orbital degeneracies[2] and adds only a small and relatively constant term to the magnetostriction, in these alloys.

Went[15] has measured the magnetostriction in Ni-Al, Ni-Si, Ni-V, Ni-Cr, Ni-Mo, Ni-W. He found that the data for these various alloys all fall on the same curve, similar to the curve for Ni-Cu alloys in Fig. 6, when plotted against the saturation magnetization instead of the electron concentration. This may be explained in the following way. In these alloys, the difference of valence between the components is too large for the rigid band model to be valid.[17] For example, they do not follow the Slater-Pauling curve for the saturation magnetization. The strong repulsive impurity potential splits localized states off the top of the $3d$ band.[17] If these states are sufficiently far above the top of the band, their only effect is to reduce the total number of states available in the band, and to decrease the bandwidth. The density of states in the band remains the same as before.[19] As the localized states of both spin directions are empty, the zero-temperature saturation magnetization of the alloy is a reliable index of band filling. Therefore, the rigid band model may often be used in these nickel alloys, provided the saturation magnetization replaces the electron concentration. Went's results are good evidence that band theory is adequate to treat the magnetostriction of alloys. The orbital degeneracy R comes at the Fermi level for a magnetization of 0.9 Bohr magneton per atom, and is therefore below the Fermi level of all of these alloys.

The behavior of Ni-Mn alloys is more complicated,[15,17] probably because the localized states remain in the neighborhood of the Fermi level, or because of a tendancy to antiferromagnetic ordering.

CONCLUSIONS AND FINAL REMARKS

It has been shown that the magnetostriction should change sign when an orbital degeneracy split by spin-orbit interaction goes through the Fermi level of a ferromagnetic alloy. This is related to the fact that the magnetostriction is proportional to the energy shifts produced by spin-orbit interaction on the $3d$ states located at the Fermi level. Such a change of sign is indeed observed[14–16] in the saturation magnetostriction of polycrystalline Co-Ni and Fe-Ni alloys, corresponding to an electron concentration of 27.7 e/atom.

This change of sign of the magnetostriction is of some technological importance, as it is the reason for the high permeability of permalloy[20] and of similar alloys.

ACKNOWLEDGMENT

The author would like to thank Professor S. A. Friedberg for his encouragement in this work.

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[20] R. Bozorth, *Ferromagnetism* (D. Van Nostrand, Inc., Princeton, New Jersey, 1951).