shows that the slope of linewidth versus temperature for the dominant three-magnon confluence process is proportional to k. In magnitude, the slope is 30% higher than predicted by theory. Cases 2 and 3 are much higher than theory, reflecting the discrepancies in their region of Fig. 2. The slopes observed for these cases point to the excitation of higher-k spin waves as mentioned previously with case 2 having a higher slope corresponding to the greater range of k available at the energy of the corner position. Figure 3 also shows the three curves intercepting the temperature axis at $T = 0\,^\circ\mathrm{K}$. In the treatment of Sparks,[9] which does not employ the high-temperature approximation, it is shown that a $T = 0\,^\circ\mathrm{K}$ intercept on a plot of this type is only a good approximation for $\vec{k}$ greater than a value given in his theory. For the case of EuS this value corresponds to an intercept of 0.5 °K for case 1, owing to the breakdown of the high-temperature approximation for the spin waves which interact with the excited state. For cases 2 and 3, it appears, from the magnitude of the linewidth, that the spin waves actually excited in this experiment have a value of k comparable to case 1 or have a value of θ different from 90°. In this case, the high-temperature approximation for all spin waves involved in the relaxation can be valid and the $t = 0\,^\circ\mathrm{K}$ intercept seen in Fig. 3 can be understood.

IV. CONCLUSION

Although experimental difficulties exist, it appears that the spin-wave relaxation in EuS is explained by three-magnon processes. These processes can account for the variation in linewidth with spin-wave parameters as the spin-wave spectrum is swept. They also predict the linear temperature dependence for the linewidth of a given spin wave, which is observed from 2 to 6 °K. This leads us to the conclusion that simple spin-wave theory, with the inclusion of two- and three-mangon terms from the dipole-dipole interaction, provides a satisfactory explanation of spin-wave relaxation in the low-$\vec{k}$ portion of the spin-wave spectrum even in the high-magnetization low-exchange materials where the interactions are very strong.

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Approach to Magnetic Saturation in the Vicinity of Impurity Atoms

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Ritz-method calculations are used to estimate the angles between applied magnetic fields of the order of 10^3 Oe and the magnetization in the vicinity of W or Nd impurity atoms in Fe or Ni. It is assumed that the impurity atom is substitutional and that its main effect is the magnetostriction, due to the mechanical strain caused by introducing an atom having a different size from that of the other atoms in the lattice, but it is shown that magnetostatic effects, caused by introducing a nonmagnetic atom, might also be important. Radii of free atoms are used, and because of this and other approximations used in the calculations of the various energy terms, the theoretical angles are only a crude approximation; but they do come to within a factor of 2 or so of the experimentally measured angles.

INTRODUCTION

In a previous publication[1] it has been argued that the direction of the magnetization in the immediate vicinity of impurity atoms in soft ferromagnetic materials, such as Fe or Ni, differs considerably from its direction in most of the ferromagnetic material when a magnetic field of the order of 10^3 Oe is applied. This was essentially an *ad hoc* interpretation of the experimental results of Ben-Zvi *et al.*[2] on recoiling nuclei embedded in Fe or Ni foils. According to this experiment,[2] the field at the site of the embedded nucleus is at an angle of about 30° to an applied field of about 1000 Oe, whereas magnetic measurements show that when such a field is applied to an iron or nickel foil practically all the magnetization is parallel to the field. It was therefore suggested[1] that this apparent discrepancy be removed by assuming that the magnetization in the vicinity of an impurity atom, which is the quantity measured in the Ben-Zvi *et al.* experiment, behaves differently from the average magnetization which affects the magnetic measurements. A semiquantitative argument indicated that the difference between the vicinity of the embedded nucleus and the rest of the ferromagnetic material could possibly be accounted for by mechanical strains, via magnetostriction. It was argued[1] that these strains could be due to dislocations, interstitials, and vacancies created by the recoil nucleus in the vicinity, or simply due to the distortion of the lattice caused by replacing an Fe (or Ni) atom by an impurity atom of a different atomic size.

In the meantime, some experimental evidence has been published[3] indicating that the radiation damage in Fe, and probably in other metals too, is generally unimportant. Unlike implantation into Ge or Si, which causes a high degree of disorder, most of the ions implanted into Fe are located within one Thomas-Fermi screening distance (i.e., ~ 0.1 Å) from the Fe lattice sites, and so, apparently, are most of the Fe atoms which are initially knocked out of their sites.[3] Although dislocations, and other lattice defects, are not completely ruled out by these experiments, there are indications of a relatively perfect lattice after a transient time of the order of 10^{-12} sec.[3] Therefore, one can rather safely assume that if there are strain effects at the implanted ion sites, these are just due to the introduction of a different atomic size into an otherwise perfect lattice.

It thus seems worthwhile to try an actual quantitative study of the suggested mechanism to see if it can yield the angle measured in the Ben-Zvi *et al.*[2] experiment. However, the rigorous problem is too complicated and contains too many unknown parameters. Therefore, no attempt at rigor will be tried here, and only a rough estimate will be obtained, based on a relatively simple approximation. The approximation is based in the first place on the assumption of a continuous material, which is a rather risky assumption when one is interested in the immediate vicinity of the impurity atom, on an atomic scale. Even for this continuous-material approximation, the energy will not be minimized for all possible configurations of the magnetization, but rather the Ritz approximation will be used, in which a certain functional form is assumed, and the energy is minimized only with respect to certain parameters (one parameter in the case studied here). But at least the approximation of the linearized theory will *not* be used here, since this has been shown[1] to be of very doubtful validity for our problem, which will be more clearly seen in Sec. II. We choose the *form* obtained from the leading terms in the linearized-theory approximation, but the energy for this functional form is then calculated rigorously, in the sense that the linear approximation is not used; yet the exchange is neglected, and the magnetostatic self-energy is somewhat modified, for reasons which will be discussed in Sec. III. A further approximation is involved in the calculation of the actual angle from the Ritz-method results, which will be discussed in Sec. IV.

Because of all these approximations, the results presented here cannot be regarded as more accurate than an order-of-magnitude estimate. Yet, none of the approximations seems so bad that it should lead to the wrong order of magnitude. In this respect it is very encouraging to see that the numerical results obtained from these approximations are of the correct order; actually they come to within a factor of 2 of all the experimental results obtained so far. Moreover, in a recent experiment, to be discussed in Sec. V, W was implanted into an alloy with very low magnetostriction, and the angular distribution was practically undisturbed. This is at least a qualitative verification of our main assumption that magnetostriction is the most important factor.

II. MAGNETOSTRICTIVE AND FIELD ENERGIES

A. General

Consider a continuous and isotropic material in which an atom of radius r_0 is removed, and an atom having a radius $r_0+\delta r_0$ is inserted in its place. A standard metallurgical technique[4] is to assume a point force, and obtain its amplitude from the change in volume. One then finds that the only nonvanishing displacement component, in polar spherical coordinates, is[4]

$$u_r = \tfrac{1}{3}\, U (r_0/r)^2\, \delta r_0 \quad , \tag{1}$$

where

$$U = (1+\nu)/(1-\nu) \quad , \tag{2}$$

and ν is the Poisson's ratio of the host material. This approach has been used successfully not only for interpreting metallurgical propeties, but also for other physical problems, such as the effect of impurities on resonance linewidth,[5] and therefore seems adequate for our purpose.

For lack of any better data, we shall use atomic radii of free atoms.[6] These are listed in Table I, and it is clear that they should be regarded as

TABLE I. Atomic diameters (from Ref. 6) used in the numerical computations of this work.

Atom	Fe	Ni	W	Nd
Diameter (Å)	2.52	2.49	2.82	3.63

crude estimates only. For the Poisson's ratio of iron, one can find in the literature various values which depend on the composition. Rather than enter these fine details, we shall use a ν of 0.3 for both Ni and Fe (Table II).

B. Ritz Functional Form

The interaction between elastic strains and magnetization in cubic crystals is formally taken into account to a first-order approximation by adding to the other energy terms the following energy density term[7]:

$$E_s = B_1(\alpha^2 e_{xx} + \beta^2 e_{yy} + \gamma^2 e_{zz}) + B_2(\alpha\beta e_{xy} + \beta\gamma e_{yz} + \gamma\alpha\, e_{zx}). \tag{3}$$

Here B_1 and B_2 are the magnetoelastic coupling constants, whose numerical values[8] are listed in Table II; α, β, and γ are the direction cosines of the magnetization vector; and the e's are the strain components. The e's are obtained by the appropriate differentiations of (1). When these are substituted in (3), one obtains, using spherical coordinates r, θ, and ϕ,

$$\begin{aligned} E_s = -Ur_0^2\,\delta r_0 r^{-3}[\,&B_1(\alpha^2 \sin^2\theta \cos^2\phi \\ &+\beta^2 \sin^2\theta \sin^2\phi + \gamma^2 \cos^2\theta) \\ &+2B_2 \sin\theta\,(\alpha\beta \sin\theta \sin\phi\cos\phi \\ &+\beta\gamma \cos\theta \sin\phi + \gamma\,\alpha\cos\theta\cos\phi)]. \end{aligned} \tag{4}$$

At least for a very large applied field, the magnetostriction works mainly against this field, which tries to align the magnetization in its direction, other energy terms being negligible. The density of the interaction energy between the applied field, $\vec{H}$ and the magnetization $\vec{M}$ is

$$E_H = -\vec{M}\cdot\vec{H}. \tag{5}$$

If it is assumed, for simplicity, that $\vec{H}$ is applied parallel to the z axis (i.e., along a crystallographic cubic axis), and if one uses the approximation of the linearized theory by assuming that H is so large that $\alpha \ll 1$ and $\beta \ll 1$, the leading term in (5) is quadratic,

$$E_H = \tfrac{1}{2} HM_s(\alpha^2 + \beta^2), \tag{6a}$$

where M_s is the saturation magnetization. On the other hand, (4) contains the linear term

$$E_s = -2Ur_0^2\,\delta r_0 r^{-3} B_2 \sin\theta\cos\theta\,(\alpha\cos\phi + \beta\sin\phi). \tag{6b}$$

Minimizing the sum of the two energy terms in (6) for the region

$$r \geq R_0 = r_0 + \delta r_0\,, \tag{7}$$

one obtains

$$\alpha = (h/H)(R_0/r)^3 \sin\theta\cos\theta\cos\phi\,, \tag{8a}$$

$$\beta = (h/H)(R_0/r)^3 \sin\theta\cos\theta\sin\phi\,, \tag{8b}$$

with

$$h = 2Ur_0{}^2R_0{}^{-3}\delta r_0 B_2/M_s\,. \tag{9}$$

It is seen that the dependence of the angle on $1/H$ is retained, as in the previous estimation[1] based on the linearized theory. Moreover, averaging $\alpha^2 + \beta^2$ over the whole material in the usual way[9] leads to a term proportional to H^{-2} in the magnetization. Such a term is always present in the approach to saturation of the magnetization[9] and is usually interpreted[10] in terms of magnetocrystalline anisotropy. For the present study it is encouraging to note that the model does not lead to a term which is not known from magnetic measurements. It should be noted, however, that a theoretical study of this H^{-2} term in the approach to saturation should include such a contribution from the strain around impurity. Also, it has already been noted[11] that an H^{-2} term can be obtained

TABLE II. Physical parameters of Fe and Ni used in the numerical computations of this work.

	Fe	Ni
Poisson's ratio ν	0.3	0.3
Magnetoelastic coupling constants (erg/cm^3) : B_1	-2.9×10^{7}	6.2×10^{7}
B_2	6.4×10^{7}	9.0×10^{7}
Compressibility C_s (atm^{-1})	6.20×10^{-7}	5.49×10^{-7}
Saturation magnetization $\pi M_s^{(1)}$ (G)	5395	1521
Change of M_s with pressure $M_s^{-1}\,\partial M_s/\partial p$ (atm^{-1})	-1.78×10^{-7}	-2.07×10^{-7}
Anisotropy constant K_1 (erg/cm^3)	4.8×10^{5}	-4.5×10^{4}

from line defects, and this seems to call for a new evaluation of this term, especially since the magnetocrystalline-anisotropy constant obtained from the approach to saturation of a polycrystalline sample does not usually agree[10] with the value of this constant obtained directly from the magnetization of single crystals.

However, if one uses the values of Tables I and II in (9), it is seen that h is at least about 10^4 Oe (for W in Fe), and up to 10^5 Oe for Nd in Ni. Clearly such values do not justify using (8), which has been obtained under the assumption $\alpha \ll 1$, $\beta \ll 1$, in order to interpret experiments done with H of 10^3 Oe or so. But one can certainly use the functional form of (8) as a basis for a Ritz-method calculations of the energy, and this is the approach adopted here.

C. Magnetostrictive Energy

In principle, the calculation should be done for different angles between the applied field and the crystallographic axes, and then the results should be averaged for the random distribution of these angles among the different crystallites of the polycrystalline material. However, for the crude approximations used here, the averaging is done in the energy terms, not in the final result. To do this, we keep the notation of the z axis as parallel to the applied field H, and assume that the crystallographic z axis is at an angle Θ_0 to this axis. Equation (4) is then rewritten in this new coordinate system, rotated by the angle Θ_0, and the expression is averaged for all possible Θ_0, as if the direction cosines of the magnetization are independent of Θ_0. This trick is an approximation for replacing each direction cosine by its average over Θ_0, and should be a good approximation if the dependence on Θ_0 is a well-behaved function. Using the components α_ρ, α_ϕ, and α_z in a *cylindrical* coordinate system, it is assumed that these are independent of ϕ, and the expression for the energy is averaged for all possible ϕ. The result of these averagings is

$$\begin{aligned}\overline{E}_s = U\frac{r_0^2\,\delta r_0}{r^3}\Big(&-B_1(\alpha_z\cos\theta+\alpha_\rho\sin\theta)^2\\&+\frac{B_1-B_2}{12}(\alpha_\rho^2-\alpha_\phi^2)(1+\cos^2\theta)\\&+\tfrac{16}{15}(B_1-B_2)\alpha_\rho\alpha_z\sin\theta\cos\theta\\&+\frac{B_1-B_2}{6}(\alpha_z^2-\alpha_\rho^2)\left[\cos^2\theta+\tfrac{7}{5}\cos(2\theta)\right]\Big)\;.\end{aligned} \tag{10}$$

In this work we choose the particular form implied by (8),

$$\alpha_\phi=0,\;\alpha_\rho=a\,(R_0/r)^3\sin\theta\cos\theta\;, \tag{11}$$

where a is the parameter with respect to which the total energy will be minimized. This form (11) now has to be substituted in (10) and then the energy density should be integrated over the volume of the whole infinite sample (7) to yield the total magnetostrictive energy. But since adding or subtracting constant terms (independent of a) to the energy should not make any difference for the minimization with respect to a, it is convenient to subtract the energy of the saturated state, $a=0$. After carrying out trivial integrations, expanding in a power series, and using tabulated[12] integrals, the difference between the energy at the state (11) and that at the saturated state is

$$\begin{aligned}W_s=\frac{2\pi}{15}Ur_0^2\,\delta r_0\Big[&-\frac{8a}{45}(7B_1+8B_2)\\&-\frac{a^2}{5}\left(\frac{B_1}{3}+\frac{B_2}{7}\right)+\frac{4}{3}(7B_1+8B_2)\\&\times\sum_{n=1}^{\infty}\frac{[(2n-1)!!]^2\,(2n+2)}{(2n-1)\,(4n+5)!!}\,a^{2n+1}\Big]\;.\end{aligned} \tag{12}$$

D. Field Energy

The density of the interaction energy of the magnetization and the applied field is given by (5), and there is no difficulty in substituting (11) in (5) and integrating over the volume of the ferromagnetic material. However, the value of the saturation magnetization M_s in the vicinity of the impurity atom cannot be the same as in the rest of the material because of at least two effects.

First, when a nonmagnetic atom replaces an iron or nickel atom in an otherwise perfect lattice, its nearest neighbors lose their exchange interaction with it. This should modify the saturation magnetization in that vicinity, as has been shown in recent years by numerous theoretical papers.[13–20] It has often been claimed that such calculations should be related to certain experiments[21–24] which revealed that there was something different in the vicinity of impurity atoms, even though there were difficulties in relating one experiment to the other[25] even from a purely experimental[26] standpoint. But whether this is so or not, the detailed calculations show[14–17] at least one thing: The change in the saturation magnetization due to this effect is at most of the order of a few percent at room temperature, and our rough model cannot deal with such fine details.

The other effect is directly related to the straining of the lattice. Because ferromagnetism depends rather critically on interatomic distances, the saturation magnetization should depend on lattice strains, and actually it is observed that the saturation magnetization changes when a pressure is applied to a ferromagnetic material.[27] Using

TABLE III. Effective pressure at $r=R_0$ due to the displacement (1), and the saturation magnetization (13) that results from it according to $\partial M_s/\partial p$ of Table II, for W and Nd impurities in Ni and Fe.

Impurity and host	Effective pressure (atm)	$\pi M_s^{(2)}$ (G)
W in Fe	0.576×10^6	−553
W in Ni	0.724×10^6	−228
Nd in Fe	2.13×10^6	−2045
Nd in Ni	2.50×10^6	−787

the compressibilities[28] of Fe and Ni (Table II), and the radii in Table I, it is seen that the change of the central-sphere radius in equivalent to a pressure of the order of 10^6 atm (see Table III). There is certainly no *a priori* reason to neglect the effect of such a pressure on the saturation magnetization.

In order to take into account the strain dependence of M_s, we have to assume that its pressure dependence is linear even up to the enormous pressure involved, for lack of other dependence which can be deduced from theory or experiment. Noting that (1) should lead to a pressure which varies as r^{-3}, we take the saturation magnetization to be

$$M_s = M_s^{(1)} + M_s^{(2)} \; (R_0/r)^3 . \tag{13}$$

Here $M_s^{(1)}$ is the value measured[28] in unstrained crystals (Table II), and $M_s^{(2)}$ will be taken so that at $r=R_0$ the value of M_s obtained from (13) will be the same as the value of M_s extrapolated from its experimental pressure dependence, for a material under the pressures listed in Table III.

The problem is now well defined if one can agree on what the experimental results are, but these are, unfortunately, not so well defined. Kouvel[29] discussed the validity of various measurements, and reached the conclusion that older measurements were unreliable because they did not use a sufficiently high field to saturate their samples. In the present context, it is particularly interesting to note that it takes[29] fields over approximately 1000 Oe to saturate Fe or Ni under hydrostatic pressure of about 3 kbar. The more recent measurements all agree on a *negative* effect for Ni, i.e., a decrease in M_s with increasing pressure. The value used in Table II for Ni is read, as the room-temperature value, from the graph of Fujiwara *et al.*,[30] who plot this effect as a function of temperature.

For iron, the experimental results at high pressures show that the magnetization does not vary *linearly* with pressure. The most detailed curve of M_s versus p is given by Graham[31] for Fe with 3-at.% Si, and presumably this cannot be much different for pure Fe. According to this curve, M_s decreases linearly with pressure up to about 130 kbar. Then there is a sharper decrease, until for pressures of some 200 kbar and higher the magnetization is zero. But it is pretty well established that the bcc α-iron is transformed into fcc γ-iron or into hcp ϵ-iron, and that the transformation starts at a pressure of about 120 kbar and is completed at about 160 kbar.[32] The sharp decrease of M_s in the Graham experiment should, therefore, indicate a crystallographic transformation to these nonmagnetic iron phases, and a crystallographic transformation must be a bulk property. The whole idea of crystallographic structure loses its meaning when a few atoms are concerned, and it is difficult to conceive that such a structure of a few atoms is nonmagnetic.

Because of these difficulties, it was decided to keep (13) and to extrapolate to the higher pressures the linear dependence as measured at the lower pressures. As for the numerical value of the change in the linear region, the pressure dependence of the internal field at the nucleus is reported[33] from Mössbauer-effect measurements, which also fit[33] some NMR data, and these are a direct measurement of what we need for our calculation. A least-squares fit yielded[34] the value which we use in Table II. It is about one-half of the value which can be read from the graph of Fujiwara *et al.*[30] for Fe at room temperature, but apparently a factor of 2 is the best fit one can expect for this kind of data.

The values for the change of M_s with pressure are thus listed in Table II; for Ni the value is taken from Fujiwara *et al.*,[30] and for Fe the value is taken from Moyzis and Drickamer.[34] Using these values and the pressures listed in Table III, one obtains the values of $M_s^{(2)}$ which should be used in (13), as listed in Table III. Substituting now (13) and (11) into (5), the difference in energy (due to interaction with the field) between the state (11) and the saturated state is obtained by integrating E_H over the volume of the whole infinite material. The result is

$$W_H = \frac{4\pi}{3} HR_0^3 \sum_{n=1}^{\infty} \frac{[\,(2n-1)\,!!\,]^2 a^{2n}}{(2n-1)(4n+1)!!} \times \left(\frac{M_s^{(1)}}{2n-1} + \frac{M_s^{(2)}}{2n} \right) \quad . \tag{14}$$

III. OTHER ENERGY TERMS

A. Magnetocrystalline Anisotropy

For a coordinate system which is parallel to the cubic axes, the magnetocrystalline-anisotropy energy density of a cubic crystal is usually written in the form[35]

$$E_K = K_1 (\alpha^2\beta^2 + \beta^2\gamma^2 + \gamma^2\alpha^2) , \tag{15}$$

where the next term with K_2 is neglected here. The room-temperature values of the constant K_1 in Fe and Ni are listed in Table II. For a polycrystalline sample with a random distribution of the directions of crystallographic axes, the same procedure of approximate minimization is used as for the magnetostrictive energy in Sec. II C: Equation (15) is written for a coordinate system rotated at an angle Θ_0 with respect to the crystallographic z axis, and then averaged over ϕ and Θ_0, assuming that α_ρ, α_z, and α_ϕ are independent of ϕ and Θ_0. This leads to

$$\overline{E}_K = (K_1/40)\,[\,4(\alpha_\phi^2 - \alpha_\rho^2) + 7(\tfrac{1}{3}\alpha_\rho^4 + 2\alpha_\rho^2\alpha_\phi^2 - \alpha_\phi^4)] \;. \tag{16}$$

Substituting from (11) and integrating over the volume, one obtains

$$W_K = (4\pi K_1 R_0^3/225)(-a^2 + a^4/27) \;. \tag{17}$$

This treatment assumes that K_1 does not change with pressure. There have been some attempts[36, 29] to calculate some pressure dependence of K_1 from experimental magnetization curves. But the technique is very doubtful, and at any rate, such a treatment should include the contribution from magnetostriction, which we consider separately. If there were some reliable experimental data on the effect of pressure on K_1, it would have been very simple to introduce them into the calculation by assuming a radial variation of this constant, like M_s in (13), but such data are not available.

B. Exchange Energy

The expression which is usually used for the exchange-energy density in the approximation of a continuous matter is[35]

$$E_e = \tfrac{1}{2}\,C\,[\,(\nabla\alpha)^2 + (\nabla\beta)^2 + (\nabla\gamma)^2], \tag{18}$$

where the exchange constant C is approximately 2×10^{-6} erg/cm, both for Fe and for Ni. For the highly strained material one can write, analogously to (13),

$$C = C_1 + C_2\,(R_0/r)^3, \tag{19}$$

and use for C_1 the value of C in an unstrained crystal. C_2 is determined, similarly to $M_s^{(2)}$, by the requirement that C of (19) has at $r = R_0$ the same value of C in a crystal under the pressure listed in Table III. There are no direct measurements of C as a function of pressure, but one can deduce it from the dependence[35] of C on the lattice constant and on the Curie temperature. The change of the lattice constant with strain can be directly obtained from the displacement (1). The change of the Curie temperature with pressure was measured.[37]

However, even a rough estimate can immediately show that using (11) in (18), with or without the use of (19), will lead to energies which are much larger than all the other energies considered in this work. This does not necessarily mean much, because calculations of domain-wall energies[38–40] usually show that for a reasonably smooth spatial variation of the magnetization the exchange energy is much smaller than other energy terms; but some kinks that hardly change the other terms can make the exchange energy calculated from (18) much larger than other energy terms. Actually, it can take a small modification of the functional form of a Ritz-method calculation to change the exchange from an infinite to a negligible value.[41] The reason for this rather strange behavior of the exchange energy is that (18) was derived[35] from a first term of a Taylor series, assuming a very slow variation of the magnetization, and just cannot be used when large variations of the magnetization take place in a small volume, as in (11) in the vicinity of $r = R_0$.

It has been argued[42] that (11) can be rather safely used in problems where one is looking for the absolute minimum of all possible functional configurations, because on a microscopic scale an abrupt change in the magnetization means that certain pairs of spins have an energy which is larger by orders of magnitude than other pairs, and such a distribution cannot be conceived as an energy minimum. It was remarked, however,[42] that such an argument does not hold in the vicinity of crystal imperfections and when one is looking just for an estimate, as in the Ritz-method calculations employed here. Moreover, in the present case, the nearest neighbors to a nonmagnetic impurity do not have one of the neighboring spins to exchange-interact with. This can be expressed as a surface anisotropy,[43] and it is usually claimed that this surface anisotropy can be neglected because it affects only the few spins near the surface.[43] But in this particular problem, it is mainly those few spins near the "surface" that we are interested in.

Since all these points have never been checked quantitatively, it seemed worthwhile to try and see how good an approximation (18) is for the particular case (11). In order to do this, a bcc lattice with a lattice constant $a_0 = 2.8606$ Å, as in iron, was considered. The spins on the lattice sites were assumed to be classical vectors having the directions implied by (11), where r is the distance of the lattice site from the impurity atom (assumed to have no spin), and R_0 was taken as 1.41 Å. The exchange energy between spins $\vec{S}_i$ and $\vec{S}_j$ was taken as[35]

$$W_{ij} = -\,2J\,\vec{S}_i\cdot\vec{S}_j\,, \tag{20a}$$

where J is related to the exchange constant, mentioned in the foregoing, by[35]

$$S^2 J = \tfrac{1}{4} a_0 C . \qquad (20b)$$

This energy was summed for all possible combinations of nearest neighbors $\vec{S}_i$ and $\vec{S}_j$. The convergence of the sum was very rapid, and spins at lattice sites a few lattice constants away from the impurity atom already made a negligible contribution to the total sum.

Computations were done for various values of the parameter a in (11), and each of these computations was done twice: once under the assumption of an undistorted cubic lattice with a constant C, and once by approximating the effect of strain as in (19), with the appropriate modification of (20). For the values of a tried, these two cases always gave the same exchange energy to within a few percent. On the other hand, the energy obtained from (18) was one to two orders of magnitude larger than the energy obtained from (20). The use of (18) is thus definitely impossible for the case studied here, and more misleading than the dropping of the exchange energy altogether. Neglecting the exchange energy might mean that the wrong r dependence is used in (11), and, therefore, the results cannot be more than a crude order-of-magnitude estimation. However, it should be noted that in the rather similar problem of the energy of a Bloch wall, rigorous two-dimensional computations[44] gave results which came within a factor of 2 or so of the original crude one-dimensional estimations which had used an approach similar to the one used here.

C. Magnetostatic Self-Energy

If the impurity atom were considered to be a nonmagnetic cavity in the ferromagnetic material, one could take the magnetostatic self-energy involved from the calculations of Humphreys and Rhodes,[45] since (11) here is a particular case of the functional form they use for the magnetization, which was even extended later[46] to a more general case, with more parameters, for the study of actual cavities. However, for a series expansion in powers of a, results are reported[45, 46] up to second order only, and there is an error in the published[45,46] results. Besides, if one wants to assume (13), the whole potential problem is modified and has to be reevaluated.

We shall, therefore, start by the evaluation of the magnetostatic potential of the volume and surface charge. In the general case, when M_s is a function of r, this potential V in a ferromagnetic material with a cavity of radius R_0 should be the solution of

$$\nabla^2 V = 0 \text{ for } r < R_0 \qquad (21a)$$

$$= 4\pi \left[\left(\cos\theta \frac{\partial}{\partial r} - \frac{\sin\theta}{r} \frac{\partial}{\partial \theta} \right) M_s \alpha_z + \left(\sin\theta \frac{\partial}{\partial r} + \frac{\cos\theta}{r} \frac{\partial}{\partial \theta} + \frac{1}{r \sin\theta} \right) \alpha_\rho M_s \right]$$

$$\text{for } r > R_0 . \qquad (21b)$$

The boundary conditions are the regularity of V for $r \to 0$ for $r \to \infty$, continuity at R_0, and a discontinuity in the derivative, given by

$$\left(\frac{\partial V}{\partial r}\right)_{r = R_0 + 0} - \left(\frac{\partial V}{\partial r}\right)_{r = R_0 - 0}$$

$$= 4\pi M_s \left(\alpha_z \cos\theta + \alpha_\rho \sin\theta \right) . \qquad (22)$$

Substituting (11) and (13) into (21) and (22), one can write the potential in the form

$$V = 4\pi \left[\textstyle\sum_n M_s^{(1)} f_n(r) + M_s^{(2)} g_n(r) \right] P_{2n+1}(\cos\theta) R_0 . \qquad (23)$$

where f_n and g_n are certain polynomials which can be obtained by not-too-complicated integrations. This potential can now be used in the conventional expression for the magnetostatic self-energy density,

$$E_M = \tfrac{1}{2} \vec{M} \cdot \nabla V . \qquad (24)$$

Substituting from the foregoing and carrying out the integrations for the whole infinite material, $r > R_0$, one obtains

$$W_M = \pi^2 R_0^3 \sum_{n=1}^{\infty} a^n \left(A_n {M_s^{(1)}}^2 + B_n M_s^{(1)} M_s^{(2)} + C_n {M_s^{(2)}}^2 \right) , \qquad (25)$$

where

$$A_1 = B_1 = \tfrac{16}{45} ,\; C_1 = \tfrac{8}{45} ,\; A_2 = \tfrac{8}{63} ,\; B_2 = \tfrac{268}{2835} ,\; C_2 = \tfrac{176}{8505} ,$$

$$A_3 = -\tfrac{16}{4725} ,\; B_3 = -\tfrac{304}{22\,275} ,\; C_3 = -\tfrac{148}{17\,325} . \qquad (26)$$

Formally, this is the magnetostatic self-energy of a continuous ferromagnetic material whose magnetization varies according to (11) and (13) around a nonmagnetic spherical cavity whose radius is R_0. For a *continuous* material with strictly localized magnetization it is well defined, but one should be careful not to push the approximation of continuity too far, and the idea of a cavity of one atomic size seems rather strange, especially if one tries to imagine the surface charge on the inner surface of such a cavity. On an atomic scale the magnetization distribution might be quite complex[47] even in pure Fe without the impurity atom, so that it is difficult even to define the cavity there; and when such a cavity is introduced, the magnetic-charge distribution in the vicinity can probably readjust itself to compensate for the "surface charge." In any case, the "cavity" cannot be quite nonmagnetic if there is some contribution from the polarization[48] of the *conduction* electrons.

From this argument it can be concluded that, whereas the magnetostatic self-energy due to the *volume* charge can be well approximated by a continuous-material calculation, the contribution of the surface charge obtained from such a calculation is most probably wrong, even as an order-of-magnitude estimate. However, in order not to jump to the wrong conclusions, it was decided to do all the computations twice: once for the magnetostatic self-energy as obtained in the foregoing for a formal cavity, namely, (25) and (26); and once for the case in which the contribution of the surface charge is artificially removed from the magnetostatic *potential*. For the latter case, one has to solve (21), but replace (22) by the artificial assumption that $\partial V/\partial r$ is continuous on $r = R_0$, keeping the other three boundary conditions the same as in the previous case. After carrying out the integrations, one obtains again the same form of (25), only with

$$A_1 = C_1 = 0,\ B_1 = -\tfrac{8}{45},\ A_2 = -\tfrac{32}{4725},\ B_2 = -\tfrac{212}{2025},$$

$$C_2 = -\tfrac{272}{6075},\ A_3 = \tfrac{368}{11025},\ B_3 = \tfrac{15\,544}{363\,825},\ C_3 = \tfrac{12\,076}{1\,091\,475},$$

$$A_4 = \tfrac{8}{18\,711},\ B_4 = -\tfrac{466}{3\,274\,425},\ C_4 = -\tfrac{5\,296}{16\,372\,125},\ \text{etc.} \qquad (27)$$

IV. RESULTS

The various energy terms which were calculated in Secs. II and III should now be combined in order to obtain the total difference in energy between the assumed configuration (11) and the state of saturation,

$$W_T = W_s + W_H + W_K + W_M \ . \qquad (28)$$

This total energy W_T is now minimized with respect to the amplitude a of the configuration (11) in order to obtain the value of this parameter.

Evidently, a small value of a means the material is almost saturated in the direction of the applied field, while a large value of this parameter indicates that a considerable portion of the magnetization is not aligned with the applied field in the vicinity of the impurity atom. We therefore define an angle Θ between the direction of the applied magnetic field and that of the average magnetization on the sphere $r = R_0$ by the relation

$$\sin\Theta = (\langle \alpha_\rho^2 + \alpha_\phi^2 \rangle_{r=R_0})^{1/2}. \qquad (29)$$

For the particular case (11), one obtains, by carrying out the averaging in (29),

$$\sin\Theta = (\tfrac{2}{15})^{1/2} a \ , \qquad (30)$$

and this angle will therefore be used in plotting the numerical results. For the order-of-magnitude estimation it should be good enough.

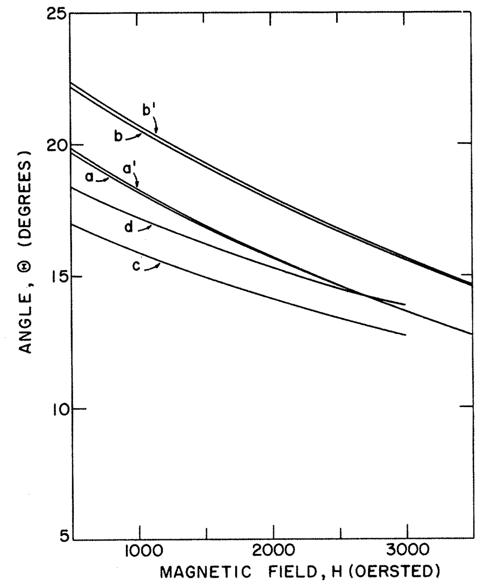

FIG. 1. Theoretical absolute values of the angle between the direction of the applied magnetic field H and the direction of the magnetization in the vicinity of a W impurity atom in Fe plotted as a function of the magnitude of H. In a and b the surface charge on the surface of the cavity is neglected, and in c and d it is included. In a and c the value of $M_s^{(2)}$ is taken as in Table III, while b and d are for $M_s^{(2)} = 0$. Curves a' and b' are the same as a and b, respectively, except that they contain the magnetostatic terms in a^4 which are neglected in a and b. The actual angle as defined in (30) is positive for a, a', b, and b', and is negative for c and d.

Angles thus obtained from (30), by using the value of a which minimizes (28), are plotted in Fig. 1 as a function of the applied field H for the case of a W impurity atom in an iron lattice. Curve a in this figure is obtained by using the value of $M_s^{(2)}$ from Table III and the constants (27) in (25), which means ignoring the surface charge of the spherical cavity whose radius is R_0. Since only a few magnetostatic terms can be calculated fairly easily, one might wonder if the effect of the remaining terms is not too large to be ignored. In order to demonstrate the difference, curve a', which has been computed without the fourth-order terms A_4, B_4, and C_4 of (27), is also plotted.

It has been mentioned in Sec. II D that different experiments on the effect of pressure on the saturation magnetization do not agree very well, and therefore the values of $M_s^{(2)}$ in Table III, which are calculated from these measurements, should be very inaccurate. It is thus important to know that the results do not depend too critically on the values of Table III. In order to check this point, the computations were repeated using $M_s^{(2)} = 0$, and the results are plotted as curve b in Fig. 1. It is

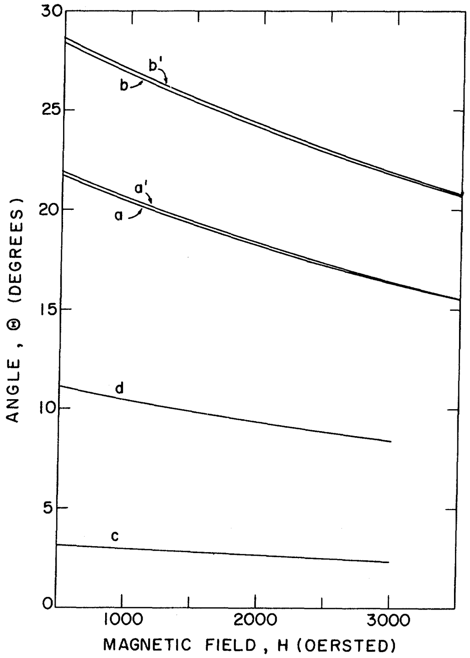

FIG. 2. Same notations as in Fig. 1 for the vicinity of a Nd impurity in iron.

very encouraging to see that the results are rather insensitive to changes in this parameter, $M_s^{(2)}$. The curve b' is analogous to a' and is obtained by neglecting the fourth-order terms in (27).

In all these curves, (27) has been used in the expression for the magnetostatic self-energy (25). If one introduces the surface charge required by a formal continuum theory, Eq. (26) should be used instead of (27) in (25). Computations for this case lead to curve *c* in Fig. 1 if the value of $M_s^{(2)}$ from Table III is used, and to curve *d* of the same figure if $M_s^{(2)}$ is assumed to vanish. It should be noted, however, that for these two cases the parameter *a* which minimizes the energy is *negative*, and its absolute value was used for obtaining the angle Θ in (30). The point is that although both the strain and magnetostatic energy terms try to pull the magnetization away from the direction of the applied magnetic field, they pull in different directions and their effects *subtract* if (26) is used. For the particular parameters used in Fig. 1 (i.e., W in Fe), it just turned out that the surface-charge contribution to the magnetostatic self-energy is about twice the contribution of the magnetoelastic term; therefore, the subtraction (curve *c*) leads to roughly the same magnitude of the angle as the removal of the surface charge (curve *a*).

Figure 2 is a plot of similarly obtained angles as a function of the applied field *H* for the case of a Nd impurity atom in an Fe lattice. The notations of the various curves are the same as in Fig. 1, and it is seen that when the surface charge is ignored – namely, when (27) is used – the angles for the Nd impurity are not much different from the angles at the W impurity. On the other hand, when (26) is used, one obtains small angles – in particular, in curve *c*. This happens because the contribution of the surface charge to the magnetostatic self-energy is opposite in sign and almost equal in magnitude to the magnetoelastic energy, so that these contributions very nearly cancel. This became very obvious from the various energy terms computed during the minimization process, and it was seen that two large numbers had actually been subtracted to obtain a much smaller one. Therefore, the small values depend too critically on the accurate calculation of the two energy terms, none of which has been calculated here very accurately, and can easily change very much with relatively small changes in the parameters which are only roughly known, e.g., the radii in Table I. This is also seen from the effect of $M_s^{(2)}$, i.e., the relatively large difference between curves *c* and *d* in this figure.

In principle, there is a simple way of distinguishing between the predictions of (27) and those of (26); and this works best for W (Fig. 1) because there the curves are close enough and a high accuracy is therefore not necessary. To do this, one should be able to switch off the magnetostriction of the material. If this is done, and if the magnetoelastic energy is the most important term, as is assumed in the derivation of curve *a*, the angles should drop to very small values for the same magnetic fields. On the other hand, if the theory leading to curve *c* holds and the terms subtract, a switching off of the magnetostriction will lead to a considerable *increase* in the angles for the same field, *H*.

Of course, it is not possible to switch off the magnetostriction in a given material, but measurements can be made on a Ni-Fe alloy in the vicinity of 80-at.% Ni where the magnetostriction passes through zero[49] or at least is[50] very small. Such measurements are being carried out by Goldring and his group,[51] and the results are in accordance with curve *a* of Fig. 1, as will be discussed in Sec. V.

Computations similar to those reported Figs. 1 and 2 were also tried for W or Nd in Ni, using the parameters of Tables I–III. However, in all the cases corresponding to the various curves in Figs. 1 and 2, no energy minimum was found, and the lowest energy was for the maximum allowable value of (11), namely, a = 2, which corresponds, according to (30), to an angle of about 47°. More refined calculations for W in Ni, taking into account the particularly large reduction of the Ni moment in the vicinity of W, will be published elsewhere.

V. DISCUSSION

It is not the purpose of this paper to present any clear-cut results of a rigorous theory. Rather, it is meant to serve as an indication to the validity of an approach to a very complex problem which, hopefully, other researchers will be able to follow, and to improve to a stage of a satisfactory physical theory. In this respect, it is sufficient to note that an order-of-magnitude estimate led to the correct order of magnitude to account for the experimental results, which were[2] 36° ± 2° for W in Ni, 30° ± 6° for W in Fe, and 24° ± 6° for Nd in Fe at a field of about 1 000 Oe. The theoretical results around this field are close enough to these values, in view of all the approximations used.

The field dependence of the angle, in the range of field values computed here, might be too small, but not very much so. The only experimental datum these graphs can be compared to right now is a single measurement on W implanted in Fe in a larger applied magnetic field. This field was approximately 3 000 Oe, but with a high degree of uncertainty because it was measured with a relatively large probe between small pole pieces. In this field, the angle between the direction of the applied field and that of the field at the site of the W nucleus was almost, but not quite, too small to be measured.[51] This probably implies a considerably stronger field dependence of the angle than in Fig. 1. But the fit seems good enough for an order-of-magnitude estimate.

One of the main drawbacks of the theory is the leaving out of the exchange energy, because if this energy term turns out to be large in spite of the arguments presented in Sec. III B, the theoretical angles will be much reduced. Hopefully, this approximation is more or less compensated by the use of the Ritz-method approximation, which tends to calculate too small angles; because when one calculates the field necessary to remove the magnetization from the energy minimum under certain constraints, one is never sure if there is not any deeper minimum somewhere which takes a higher field to get out of. The approximation involved in calculating the magnetostrictive energy from a continuous-material model should be good enough, since it is used successfully in other[5] physical problems. However, the *radii* of Table I used in the *numerical* computations of this model are rather doubtful.

It has been suggested in Sec. IV that the role of magnetostatic self-energy, which is very difficult to decide from theoretical considerations be found from a measurement of the angular distribution for ^{186}W implanted into a Ni-Fe alloy with low magnetostriction. The choice of W, rather than ^{148}Nd, is obvious from Fig. 2, which is too sensitive to approximations in the theory because of the subtraction of almost equal numbers, whereas the case for W (Fig. 1) is clear cut. According to this figure, if curve *a* holds, the angular distribution in an 80-at.% Ni-Fe alloy should be much *less* perturbed than in Fe or Ni. On the other hand, if curve *c* holds, the angular distribution in this alloy should be considerably *more* perturbed than in pure Ni or Fe for the same magnetic field. This argument assumes, of course, that the implanted nucleus in the alloy responds to the average properties of the ordered alloy, but this seems very likely in view of the Mössbauer-effect measurements[52] according to which the Ni nucleus is found in a hyperfine field which can be directly related to the average magnetization of the alloy.

However, since implantation into an alloy has not been tried before, there is another *a priori* possibility that the implanted W will come to rest in a vicinity which is considerably more Fe-rich or Ni-rich than the average of the alloy, and the magnetostriction will be almost the same as for pure Fe or for pure Ni. After all, Ni and Fe atoms must be knocked out of their sites by the high-energy ions entering the lattice, and they do not necessarily rearrange themselves later in the same ordered alloy configuration which they had before. There is a lot of evidence[3] that in a pure metal the atoms which have been knocked away from their sites generally return in a relatively short time to the lattice sites, although there might also be[53] some notable exceptions to this. However, in a pure metal all the atoms are equivalent and it does not make any difference which atom enters which lattice site, whereas in an alloy a rearrangement of the atoms can lead to clusters of different compositions. Moreover, such a viewpoint is supported by the observation that there is a large change in the remanence and coercive force of Ni-Fe alloys when irradiated by neutrons, whereas such irradiation hardly changes these properties in Fe or Ni metals,[54] but there might be[55] some notable exceptions here too. If this is the case, one would expect the perturbation of the angular distribution in the alloy to be about the same as, or somewhat larger than, the perturbation in Ni.

Experimental results[51] indicate that the perturbation in an 80-at.% Ni-Fe alloy is considerably smaller than the perturbation in Ni at the same field H. This is in accordance with the assumptions leading to curve *a* in Figs. 1 and 2, namely, that the most important factor determining the approach to saturation in the vicinity of impurities is the magnetostriction. It is essentially what one would expect by using just the qualitative arguments presented before.[1]

Another possible experimental checking of the theory has already been suggested,[1] namely, to repeat the neutron scattering experiment of Low and Collins,[21,22] applying a larger magnetic field because their results should change considerably if their Fe or Ni was not saturated in the vicinity of impurities.[1] It was later noted[56] that the same checking can be done by *reducing* the applied magnetic field, which is easier than increasing it. Such an experiment has recently been done in which the scattering from one sample was measured once with the magnetic-field current turned on full and once with the current reduced by a factor of 3, and there was no significant difference in scattering between the two cases.[56] Unfortunately, however, this was done for Fe impurity in Ni, which is the least significant possibility because Ni and Fe have practically the same radius and they are both magnetic, so that neither magnetostrictive nor magnetostatic contributions can be as large as for the cases discussed here. It should be more interesting to check the samples of W impurity in Ni.[57,58]

Finally, it should be noted that both this theory and the experimental results[2,51] quoted in it are at apparent discrepancy with the conclusion of Deutch[59] that the perturbed angular correlations for several rare earths implanted in iron follows the magnetization curve of iron. However, the curve of Deutch[59] does not quite follow conventional magnetization curves for iron[60] or Ni,[61] besides the possibility of a difference in sensitivity of different measurements. Yet this theory is in agreement with the findings of Deutch[59,62] and of others[63] that it takes a field of 10 000 Oe to saturate the perturbed angular-correlation effect in nuclei implanted in iron.

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Exciton–Optical-Phonon Coupling in CoF_2

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We present a theory of the temperature dependence of the frequency, linewidth, and infrared absorption strength of the E_g optical phonon in CoF_2, assuming that the coupling between the phonon and the *AD* exciton is responsible for these effects. We find that a model based on the orbit-lattice interaction can account for these phenomena. We also predict that the E_g phonon should be split by application of a magnetic field parallel to the *c* axis. We estimate the "*g* factor" associated with this splitting and find that one should be able to observe the splitting in readily attainable magnetic fields. The temperature dependence of the above phenomena in the paramagnetic and antiferromagnetic state is discussed. A point-charge estimate of the optical-phonon–exciton coupling constant produces a value much smaller than that required to fit the data.

I. INTRODUCTION

The properties of the Co^{++} ion in insulating crystals are most striking. The ground state of this ion (a d^7 configuration) has threefold orbital degeneracy in a cubic crystalline field, while the spin $S = \frac{3}{2}$. The presence of spin-orbit coupling or components of the crystalline field with low symmetry split the twelve-fold degenerate ground-state manifold into a complex of low-lying energy levels. Detailed experimental[1] and theoretical[2] study of Co^{++} placed substitutionally in MgF_2 have been carried out by Gladney. In this environment, the twelve-fold degeneracy of the d^7 ground state is split into six Kramers doublets, with excitation energies that range from 150 to 1400 cm^{-1}.

An approximate description of the electronics excited states of the Co^{++} ion in the antiferromagnet CoF_2 ($T_N = 37.7\,°K$) may be obtained from Gladney's energy level scheme for Co-doped MgF_2. In particular, Martel, Cowley, and Stevenson[3] have studied the low-lying electronic excitations in this compound. These authors find two sets of exciton levels that lie in the 150-cm^{-1} range, for $T > T_N$. The two exciton bands are referred to as the *AC* level and the *AD* level. The *AC* exciton band suffers a Davydov splitting for a general value of the wave vector $\vec{k}$, while symmetry considerations indicate that the Davydov splitting vanishes in the *AD* band,[4] in agreement with the observations.[3]

Allen and Guggenheim[5] have observed infrared (IR) absorption by an optical phonon of E_g symmetry in both the paramagnetic and antiferromagnetic state of CoF_2. The integrated strength of this line was found to exhibit a strong temperature dependence. The width of the line was also strongly temperature dependent, with a minimum at T_N, and a rather large (≈ 6 cm^{-1}) increase in the frequency of the E_g mode was observed as the crystal