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Nuclear Zeeman Effect in Gold Atoms Dissolved in Iron, Cobalt, and Nickel*

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The nuclear Zeeman effect has been observed in Au^{197} nuclei dissolved in ferromagnetic hosts, using the Mössbauer effect. The magnetic moment of the 77-keV isomeric state of Au^{197} was measured as $\mu = +0.37$ (4) nm. The hyperfine magnetic fields at Au nuclei dissolved in iron, hexagonal cobalt, cubic cobalt, and nickel were found to be -1420 (180), -980 (120), -990 (120), and -340 (60) kG, respectively, by comparison with external magnetic fields up to 86 kG. Experiments in low external fields gave an unexpected result which is interpreted in terms of magnetostriction in the ferromagnetic sources.

I. INTRODUCTION

Since the discovery in 1958 by Samoilov *et al.*[1] that large magnetic fields are induced at the nuclei of diamagnetic metal atoms dissolved in ferromagnets, these fields have been the subjects of several experimental studies.[2–17] The hyperfine fields are believed to arise from a contact interaction of the impurity nucleus with conduction *s* electrons unpaired via an exchange-polarization mechanism with neighboring magnetic atoms. Other mechanisms are possible; there are available at present no quantitative theoretical estimates of these fields.

A thorough understanding of the interactions which induce fields at the nuclei of nominally diamagnetic atoms could provide a valuable link in a theoretical explanation of ferromagnetism. Some but not all of the mechanisms responsible for ferromagnetism are present here and it is useful to study these mechanisms separately. In particular, it should be possible to study the exchange forces between unpaired electrons on magnetic atoms and conduction electrons from the diamagnetic atoms.

Until now the theoretical work in this area has been quite qualitative and the experimental work has attempted mainly to establish the mechanism by which induced magnetic fields are created. A useful experimental approach is to determine the magnitudes and signs of the induced fields at nuclei of diamagnetic impurities in very dilute solutions in iron, cobalt, and nickel lattices. A complete set of fields has been measured for tin impurity atoms.[16] We report herein a complete set of measurements on gold impurity atoms.

Several of our results have been obtained previously by different methods. In most cases, as is seen, the agreement between the previous measurements and ours is quite satisfactory. Our measurements are based on direct comparison of the internal magnetic fields with external fields and require in principle somewhat less interpretation than do the other less direct experiments. Still some assumptions are necessary, as indicated later. We feel that it is valuable when reporting internal field measurements to state clearly the assumptions involved in deriving the results from the data. Inasmuch as this has not always been done in the past, we have devoted the next section to discussion of the various experimental methods which have been used in determining internal fields in ferromagnetic metals.

II. THE VARIOUS EXPERIMENTAL METHODS

We discuss, but do not describe, each method separately. In light of the present poor theoretical understanding and the scarcity of data on induced fields it would be meaningless to classify the methods in order of merit. Our purpose is rather to point out the assumptions implicit in each method.

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A. Magnetic Resonance

This is by far the most accurate technique. It has had limited application, especially in studying induced fields, and the extent of its applicability here may not be great in the near future. The resonant atoms are those in the domain walls, and the signal is thus extinguished in large applied fields. As in all magnetic resonance experiments, one detects only those atoms which meet the resonance conditions, and one is not assured that he is observing a fair sampling of the entire specimen, (i.e., there may also be nonresonant sites). In addition, the location of the resonant atoms in the domain walls introduces some small doubt in the fidelity with which the transition frequency reflects the internal field in an atom within a domain. In practice these two disadvantages do not seem to be very serious.

B. Recoil-Free Resonance

This method (the Mössbauer effect) is, like NMR, essentially spectroscopic in nature. Unlike NMR it measures directly the hyperfine structure of nuclei within domains, and it can be used in the presence of large applied magnetic fields. Applicability is limited of course to those nuclei showing the Mössbauer effect and possessing well-resolved hyperfine structure. Present techniques provide an accuracy of about 1% at best, although higher precision is attainable.

C. Nuclear Polarization

By measuring the variation with temperature of the angular distribution of β or γ radiation from oriented nuclei one can determine the mean strength of magnetic interactions causing the orientation. It is not feasible in most cases to determine the distributions around the mean; thus, unlike the two spectroscopic methods, nuclear polarization does not allow one to decide whether there are several lattice positions with different internal fields, or only one. In addition this method is much less sensitive than the spectroscopic methods to the presence of other interactions (such as quadrupole splitting), and the presently attainable accuracy is approximately 10%. Internal fields are obtained from nuclear polarization data rather indirectly. In practice the assumptions which must be made regarding reorientation and perturbation in the intermediate nuclear state are usually borne out. The wide applicability of this method is a distinct advantage and the accuracy with which it yields internal fields is completely satisfactory in view of the present state of the theory.

All three of the above techniques can be used to determine the signs of internal fields.

D. Heat Capacity Measurements

While it yields the least information about the details of the nuclear spin Hamiltonian and cannot be used to determine the sign of the internal magnetic field, the method of heat capacity measurements at low temperatures has two distinct advantages: (1) it is generally applicable except to extremely dilute alloys, and (2) for a given internal field it provides observable results at higher temperatures than does nuclear polarization. Like nuclear polarization this method measures only the mean internal field and not the internal field distribution.

III. OTHER WORK

The first measurements on internal fields at the nuclei of gold atoms dissolved in iron were reported by Samoilov *et al.*,[1] who discovered the effect in nuclear polarization experiments on Au^{198}. They reported a hyperfine field in excess of 1.0×10^6 G. Kogan *et al.*[14] deduced a field in excess of 2.0×10^6 G from similar experiments on Au^{199}. The uncertainty in the reported magnitudes, and presumably the discrepancy, arises from the lack of a reliable thermometer in these early experiments, which utilized contact cooling to 0.03°K. Stone and Turrell have recently repeated the Au^{198} experiments in an iron sample in which Co^{60} nuclei were simultaneously polarized, thereby acting as a thermometer. They obtained an internal field of $1.6\pm0.2\times10^6$ G for Au in Fe.

Mössbauer absorption experiments on Au^{197} in Fe, Co, and Ni were reported by Roberts and Thomson[8,9] and by Shirley, Kaplan, and Axel.[5] The excited-state nuclear magnetic moment, which produced most of the splitting, was unknown, and it was not possible to deduce an internal field from the early experiments. The latter workers noted that an internal field of 0.28×10^6 G would be compatible with a magnetic moment of 1.6 nm, which is the value of the magnetic moments of several neighboring odd thallium isotopes. As discussed in Sec. IV the moment of the excited state of Au^{197} is much less than this, and the internal field is much greater.

More recently, Roberts and Thomson[18] have carried out higher resolution Mössbauer experiments in which they observed unresolved structure in the absorption lines. By fitting the data to a Hamiltonian containing an axially symmetric quadrupole interaction with symmetry axis parallel to the direction of magnetization, they derived an excited-state magnetic moment of $+0.38\pm0.08$ nm and internal magnetic fields of magnitudes 1460 ± 160 kG (Au in Fe), 1180 ± 120 kG (Au in Co), and 420 ± 120 kG (Au in Ni).

Samoilov *et al.*[4] have measured β asymmetry from polarized Au^{198} in Fe and Ni. Invoking the measured value of -1.0 ± 0.7 for the beta-decay matrix-element function λ/μ, they deduced a negative sign for the internal fields at Au nuclei in both Fe and Ni. In addition they found a ratio of 5.6:1 for the magnitudes of these internal fields with the most probable values being -1.0×10^6 G and -0.18×10^6 G, respectively.

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[18] L. D. Roberts and J. O. Thomson, Phys. Rev. **129**, 664 (1963).

TABLE I. Hyperfine fields at Au nuclei in kG.[a]

Impurity atom	Hosts			Reference
	Fe	Co	Ni	
Au^{197}	−1420 (180)	hex. −980 (120) cubic −990 (120)	−340 (60)	This work
Au^{197}	1460 (160)	1180 (120)	420 (120)	18
Au^{198}	−1000	...	−180	4
Au^{198}	1600 (200)	...	...	12
Au^{199}	>2000	...	...	14

[a] The signs of the hyperfine fields were not determined except where noted.

All of these results, along with those reported herein, are given in Table I.

IV. THE HIGH-FIELD MÖSSBAUER EXPERIMENTS

In view of the somewhat indirect nature of the above measurements and the assumptions involved in deducing internal fields from the data, a direct comparison of the internal fields with externally applied magnetic fields was highly desirable. Thus a series of experiments was performed in which the Mössbauer spectra of the 77-keV γ ray of Au^{197} in Fe, Co (cubic and hexagonal), and Ni where observed in applied magnetic fields between 0 and 86 kG. The experiments were all performed at 4.2°K using very dilute solutions of Pt^{197} in the ferromagnetic host lattices as the sources and an absorber of 5–10 mil metallic gold. A "tilted-wheel" spectrometer[19] was used for the high-field measurements; it was compared and intercalibrated with an "automatic" spectrometer.[20]

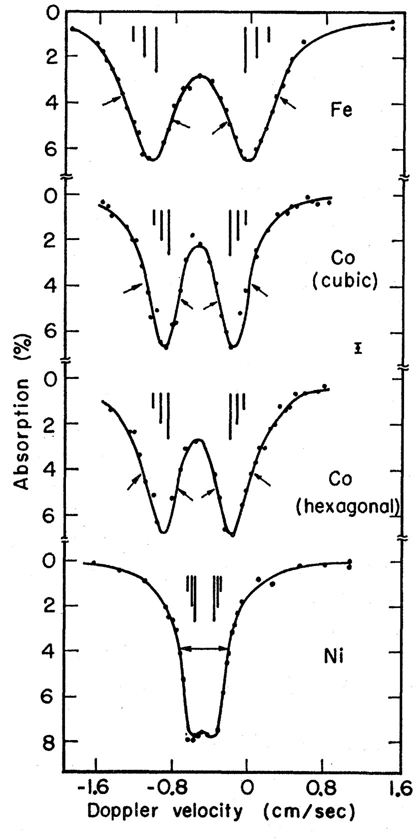

FIG. 1. Absorption spectra of Au^{197} in Fe, cubic Co, hex. Co and Ni taken in zero external magnetic field. Solid lines are the sums of six Lorentz curves with positions and intensities shown.

The sources were prepared by alloying ≤ 1 at.% of Pt (containing Pt^{197}) with the host metal at 1600°C in an argon atmosphere for ~3 h and then quickly quenching them in water. The hexagonal Co source was prepared by cold-working the alloy at room temperature; an x-ray analysis of this source showed 95±5% hexagonal Co.[21] The cubic Co source was prepared by annealing the alloy at 1300°C for $2\frac{1}{2}$ h, then slowly cooling to room temperature over a period of about 2 h. The intermediate grain size in this sample made it difficult to obtain a confirmatory x-ray analysis and the crystal structure was inferred from: (1) the transition temperature of 417°C for the fcc-hcp transition in pure Co (the cubic structure is the stable form at high temperatures[22]) and (2) a similar procedure to that described above has been used to make several dilute cobalt alloys (including Ir and Pd) for NMR studies,[23] and in each case the percentage of cubic Co was >90%.

Typical absorption spectra for Au^{197} dissolved in Fe, cubic Co, hexagonal Co, and Ni are shown in Fig. 1. These spectra are symmetrical and better resolved than those reported in Ref. 5, and are in good agreement with (but less well-resolved than) the high-resolution work of Roberts and Thomson.[18] These latter workers used gold-in-Fe (Co,Ni) absorbers rather than our Pt-in-Fe (Co,Ni) sources. The good agreement of our spectra with theirs indicates that the equilibrium local fields at Au nuclei in Fe (Co,Ni) are established within the lifetime of the isomeric state of Au^{197} (2.7 nsec).[24] The differences from the survey experiments reported in Ref. 5 may be attributed to inadequate mixing during source preparation and to poor resolution of the apparatus in the earlier experiments.

Preliminary experiments[6] showed that the change in total hyperfine splitting on application of an 86-kG magnetic field was small in every case. For Au in Fe this change was positive, and for Au in Ni it was negative. The sign was uncertain for Au in Co. Because the total change in position of either main line in the spectrum was only about $\frac{1}{20}$th of a linewidth, a more efficient method of data collection was adopted. Rather than recording the whole resonant portion of the spectrum, we concentrated on the points of maximum slope (indi-

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[20] D. A. Shirley, M. Kaplan, R. W. Grant, and D. A. Keller, Phys. Rev. **127**, 2097 (1962).

[21] We are indebted to George Gordon for performing this x-ray analysis.

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[24] *Nuclear Data Sheets,* compiled by K. Way *et al.* (National Academy of Sciences, National Research Council, U. S. Government Printing Office, Washington, D. C.).

TABLE II. Experimental results.[a]

Source	Excited-state magnetic moment[b] (nm)	Excited-state splitting $2\mu_{ex}H$ (cm/sec)	Ground-state splitting $2\mu_g H$ (cm/sec)	Hyperfine field (kG)	Ratio of hyperfine fields[c]	Chemical shifts[d] (cm/sec)
Fe-Pt (1%)	+0.34 (9)	1.29 (2)	0.36 (2)	−1420 (180)	1	−0.54 (2)
Cub. Co-Pt (1%)	+0.36 (6)	0.90 (2)	0.24 (2)	−990 (120)	0.70 (2)	−0.54 (2)
Hex. Co-Pt (1%)	+0.39 (6)	0.89 (2)	0.22 (2)	−980 (120)	0.69 (2)	−0.53 (2)
Ni-Pt (1%)	...	0.31 (2)	0.09 (2)	−340 (60)	0.24 (2)	−0.47 (2)

[a] Errors in the last place are given parenthetically.
[b] Derived from slopes of lines in Fig. 2.
[c] Ratio is defined relative to hyperfine field at Au nuclei dissolved in Fe.
[d] Chemical shift is defined relative to pure Au absorber.

cated by arrows in Fig. 1) for the Fe and Co specimens. For each sample an average of 3×10^6 events were recorded at each of the selected velocities and at several values of the applied magnetic field. The data were collected in 3 sets of 10^6 counts apiece and checked for consistency and reproducibility. For Au in Ni this procedure was not feasible because of the much poorer resolution of the two main lines. We reverted to the less accurate technique of recording the entire spectrum for each of four values of applied magnetic field. The accuracy attained in this way was poorer than for the other three alloys (Au in Fe, hex. Co, and cubic Co) and the data were used only for obtaining the sign of the internal field rather than its magnitude or the magnitude of the excited-state magnetic moment.

In Fig. 2 the change in the excited-state splitting for each specimen is plotted against the effective applied magnetic field, which is just the difference between the applied field at the source and that at the absorber (this can easily be shown by using the selection rules for a longitudinal Zeeman effect experiment). A common characteristic of all the curves in Fig. 2 is an initial increase of the total splitting with field at small fields and a linear decrease for effective applied fields above ~15 kG. The initial behavior is ascribed to magnetostriction and other effects involved in the initial orientation of the internal fields parallel to the applied field (Sec. V), and is not quantitatively understood. Such effects (including Joule magnetostriction) saturate with the magnetization in ferromagnets[25]; thus the field region above ~15 kG should be essentially free of these effects. We therefore have based our interpretation of the excited-state magnetic moment of Au^{197} and the signs and magnitudes of the internal fields only on the data above 15 kG. A stringent test of the validity of this interpretation is the requirement that the slopes in Fig. 2 for all the alloys be equal. This requirement is born out by the constancy of the magnetic moments derived from the Fe and Co data (Table II).

In all four alloys the high-field slopes are negative; thus the internal fields at nuclei of gold atoms dissolved in Fe, cubic Co, hexagonal Co, and Ni are negative. The magnitudes of the internal fields are derived from the splitting observed in the full absorption spectra taken in zero field. Using the statistically averaged value for the excited-state magnetic moment, $\mu_{ex}=0.37\pm0.04$ nm, and the measured ground-state moment of +0.14 nm,[24] the magnitudes of the internal fields were calculated and are shown in Table II (along with several other experimental results). These fields are compared with the results of other workers, where available, below.

Our value for the magnitude of the internal field at Au nuclei dissolved in Fe is in good agreement with the values reported in Refs. 12 and 18. Samoilov *et al.*'s[4] value of 1000 kG may probably be regarded as a lower limit. This value was derived by using $\lambda/\mu=-1\pm0.7$ where λ and μ are functions of β decay matrix elements, and for a value of $\lambda/\mu=-0.3$ the internal field could have been as large as 4000 kG. We have used our value of the internal field to set much narrower limits on the ratio λ/μ for the 2− (β) 2+ beta decay in Au^{198}, using their data, as

$$\lambda/\mu=-0.55\pm0.15.$$

For this range of λ/μ the magnitude of the internal field

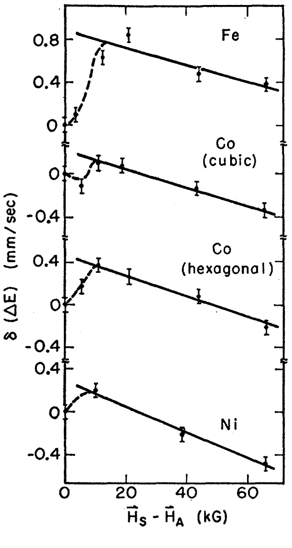

FIG. 2. Change in the excited-state splitting versus the difference in the external magnetic field at source and absorber for Au^{197} in Fe, cubic Co, hex. Co and Ni.

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[25] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951).

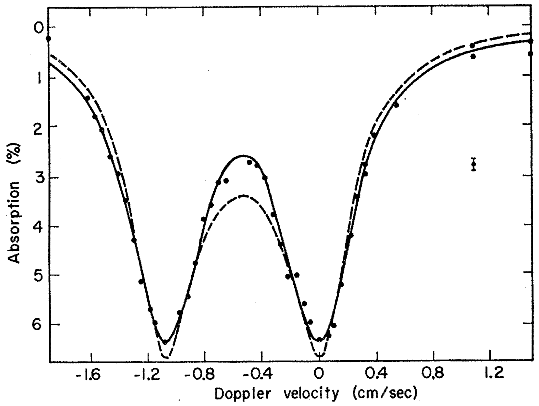

FIG. 3. Au^{197} in Fe absorption spectrum in an external magnetic field ($\mathbf{H}_s-\mathbf{H}_a=65$ kG). Solid line is "best" fit assuming magnetic moments have the same sign; dashed line is "best" fit assuming magnetic moments have opposite signs.

determined in Ref. 4 agrees with our present result. Our sign determination agrees with theirs.

Only Roberts and Thomson[18] have reported a value for the internal field of Au in Co. Their value is in good agreement with ours. We find that the fields in cubic and hexagonal cobalt are the same to within 5%, and both are negative.

The negative sign which we find for the field at Au nuclei in Ni is in agreement with the determination of Samoilov *et al.*[4] Our value of 340 kG for the magnitude of this field is between the 420 kG reported by Roberts and Thomson[18] and the 180kG of Samoilov *et al.* Samoilov *et al.*[4] found the internal fields at Au nuclei in Fe and Ni to be in the ratio 5.6:1. Nuclear polarization experiments should give this ratio more accurately than the absolute values of the magnitudes of the internal fields. Thus, if we combine this ratio with our value of 1420 kG for the magnitude of the internal field of Au in Fe, rather than using the nuclear polarization value of 1000 kG, we may derive a value of 250 kG for the magnitude of the internal field for Au in Ni, in better agreement with our result.

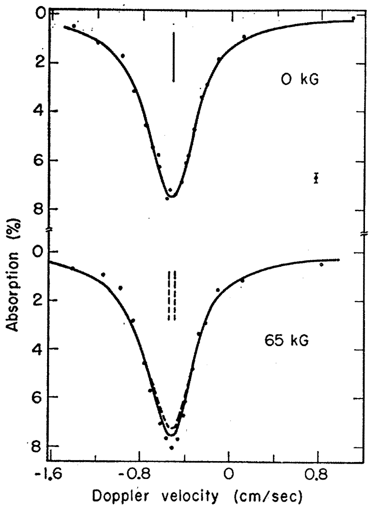

FIG. 4. Absorption spectra for Au^{197} dissolved in Be at 0 and 65 kG external magnetic fields ($\mathbf{H}_s-\mathbf{H}_a$). The solid line is the "best" fit to the data in 0 field using a single Lorentz curve. The dashed line is the theoretically expected absorption curve at 65 kG for $\mu_{77}=+0.37$ nm in the absence of any quadrupole effects.

The sign of the magnetic moment of the 77-keV excited state of Au^{197} can be deduced from a detailed comparison of some of our better resolved Au-in-Fe spectra with theoretical curves calculated for positive and negative moments. In a longitudinal Zeeman experiment the intensities of the six Zeeman components of a 1/2+ (dipole) 3/2+ transition are in the ratio 1:0:3:3:0:1 if the two magnetic moments have the same sign, and 3:0:1:1:0:3 if the moments are of opposite sign, provided that the g factor of the spin 1/2 state is much larger than that of the spin 3/2 state. We have compared theoretical Lorentz curves with one of our Au-in-Fe spectra in Fig. 3. Only the 1:0:3:3:0:1 curve fits the data acceptably, thus indicating that the sign of the excited-state magnetic moment is positive, in agreement with the conclusion of Roberts and Thomson, who carried out unpolarized experiments at considerably higher resolution and fitted their data with the 1:2:3:3:2:1 intensity ratios required by a positive excited-state magnetic moment. Our best value for the magnetic moment of the 77-keV isomeric states of Au^{197} is

$$\mu_{77}=+0.37\pm0.04\text{ nm}.$$

Experiments in large external magnetic fields were performed on dilute sources of Pt^{197} (~1 at.%) dissolved in Be and Pt in an attempt to measure μ_{77} directly. It was hoped that a single line absorption spectrum, obtained by using these sources, would be split upon the application of the external magnetic field, and the change in shape of the absorption line could be related directly to the magnetic moment. Using the Pt source, essentially no change was observed in the absorption spectrum between 0 and 65 kG effective external field. With the Be source the absorption dip seemed to increase upon the application of a 65-kG external field as shown in Fig. 4. If only a magnetic dipole interaction were present the absorption line should show a decrease in the dip and for $\mu_{77}=0.37$ nm we show the expected theoretical result as a dashed curve in Fig. 4. The experiments using Au-in-Be and Au-in-Pt sources therefore indicate a more complicated behavior than purely magnetic dipole interactions and make the extraction of a value for μ_{77} quite difficult.

We were able to explain the results of these experiments qualitatively on the basis of a mixed magnetic dipole and electric quadrupole interaction. The absorption lines observed in zero external field are about twice as wide as would be expected from purely theoretical estimates for a 5–10 mil Au absorber[5] indicating the possibility of a sizeable quadrupole interaction. A quadrupole interaction is not unexpected in this case since the ground-state quadrupole moment has been measured as $Q=+0.60\pm0.06$ b.[26] In the presence of

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[26] A. G. Blachman and Allen Lurio, Bull. Am. Phys. Soc. 8, 9 (1963).

both a magnetic field and an electric field gradient the eigenfunctions of the nuclear substates will be dependent upon the relative strengths of the two interactions and the angle between the magnetic field and the electric field gradient: We will assume that the electric field gradient tensor possesses axial symmetry with respect to some axis, z', which is not necessarily the magnetic field direction. The total interaction Hamiltonian can then be written as [27,28]

$$\mathcal{H}=\mathcal{H}_{\mathrm{mag}}+\mathcal{H}_{\mathrm{el}}=gI_zH+P[I_{z'}^2-(\tfrac{1}{3})I(I+1)], \quad (1)$$

where $g=\mu/I$, I is the nuclear spin, P is the quadrupole coupling constant and z is the direction of the magnetic field H.

Calculations were performed using the eigenvalues of mixed electric quadrupole and magnetic dipole interactions for $I=3/2$ given in Ref. 28. The nonvanishing matrix elements of the above Hamiltonian are expressed in a general form in Ref. 27. Using these matrix elements, secular determinants were obtained from which the eigenvectors corresponding to the eigenvalues of Ref. 28 were calculated. From the eigenvalues and eigenvectors the transition energies and intensities (weighted by the proper Zeeman intensities) were calculated and, after considering the purely magnetic splitting in the absorber, the spectrum of absorption lines was obtained. In the general case there will be 32 absorption lines. By choosing appropriate parameters consistent with the experimental conditions, it was possible to match the experimental results of Fig. 4. It was not possible to derive quantitative coupling constants by this procedure since the initial state of the source was not well known. The most straightforward way to investigate this problem quantitatively would be to use a single-crystal source where the orientations of the electric field gradient and magnetic field could be determined.

V. MAGNETOSTRICTION EFFECTS

The low-field behavior of the excited-state splitting for Au in Fe, Co, and Ni (Fig. 2) was unexpected and is not susceptible to a simple quantitative explanation. We have termed this a magnetostrictive effect because it saturates at large fields (10–15 kG) as would be expected for magnetostriction, which follows the magnetization in ferromagnets.[25] It is not surprising that the induced field at Au nuclei dissolved in Fe depends sensitively on small changes in the distance, polarization, or orientation of neighboring Fe atoms because the Au atoms (atomic diameter 2.80 Å)[29] are quite crowded in an Fe (atomic diameter 2.48 Å)[29] lattice and the outer electrons of gold must overlap considerably with the polarized outer electrons of iron.

While we are unable to show uniquely that this effect is related to magnetostriction, the behavior is at least qualitatively similar to this mechanism. The size of the initial increase in Fig. 2 is in the order Fe>Co>Ni. It is expected that the unpaired spin density in the outer atomic regions is in the order Fe>Co>Ni. Therefore, if the change in electronic overlap between Au and the Fe, Co, and Ni atoms is roughly the same, this would account for the relative sizes of the observed effects. Joule magnetostriction in Fe, Co, and Ni saturates in the same direction, which correlates with the fact that we observe an initial increase in splitting in every case in Fig. 2. It seems unlikely, however, that Joule magnetostriction alone could account for effects of this magnitude, and orientation effects on an atomic scale are indicated.

VI. THE NUCLEAR MODEL FOR Au^{197}

Braunstein and de-Shalit[30] have proposed a core-excitation model to explain the spectroscopic properties of Au^{197}. We discuss in detail below the relationship of the Mössbauer resonance experiments to this model.

The basic premise in the core-excitation model is that an odd-A nucleus may be excited either by promotion of the unpaired odd particle to a higher spectroscopic state or by excitation of the paired even-even core, which couples in its excited state with the odd particle. The exact nature of this excitation is unspecified in the model, which is as yet only phenomenological. In Au^{197} the odd (79th) proton is thought to be in a $2d_{3/2}$ shell-model state, which accounts for the spin and magnetic moment of the ground state. In the core-excitation process the even-even core acquires the spin and parity 2+, which is observed as the first excited state in almost all even-even nuclei. This excited core then couples with the $d_{3/2}$ proton to form states with spin and parity assignments 1/2+, 3/2+, 5/2+, and 7/2+. Braunstein and de-Shalit have identified these levels among the low-lying excited states in Au^{197}. In particular the first excited state at 77 keV was given the assignment $|j_p=3/2, j_c=2, J=1/2\rangle$, where the j's denote, respectively, the particle, core, and total angular momentum. From experimental transition probabilities these authors estimated the g factor of the core as $g_c=+0.64\pm0.04$, and the estimated magnetic moment of the 77-keV excited state was $+0.60\pm0.04$ nm, in fair agreement with the preliminary experimental value[6] of 0.4 ± 0.1 nm but well outside the limits of error on our present value of $+0.37\pm0.04$ nm. In fairness to the model we should make two points: (1) This model is unique in predicting a magnetic moment considerably below 1.0 nm in a straightforward way. Any single-particle shell model calculation would give a magnetic moment between the Dirac line (+1.0 nm in this case) and the Schmidt line (+2.79 nm) for an $s_{1/2}$ proton. Even if configuration mixing is invoked it is not practicable, using reasonable

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nuclear parameters and few configurations, to calculate a magnetic moment as small as the experimental value. Of course it is always possible in principle to calculate any type of collective behavior using pure $j-j$ coupling (or any other poorly chosen basis) if enough configurations are included. This is a fundamental feature of quantum mechanics and in no way does it reflect credit on the single-particle model. In many cases, including this one, we believe, it is more enlightening to think of the excitation as a collective effect. (2) Braunstein and de-Shalit showed that the magnetic moment of the 77-keV state is given, in the core-excitation model, by

$$\mu_{1/2}=g_c-\tfrac{1}{2}g_p\,, \tag{2}$$

where g_c and g_p are the g factors of the excited core and the odd proton, respectively. The quantity g_p is just the g factor of the same odd proton found in the ground state ($g_p=+0.093$) and there is little leeway in choosing a value for g_p. Several approaches are possible in estimating g_c. The authors in Ref. 30, in an effort to test quantitatively the internal consistency of their model, estimated g_c from measured $M1$ transition probabilities. This procedure has the advantage of requiring no adjustable parameters. A disadvantage is that the accuracy of a g factor estimated in this way is not high. A somewhat more empirical alternative is to set $g_c\approx Z/A$ as was done in the earlier estimates of the core g factor of deformed nuclei. This procedure yields $\mu_{1/2}=+0.36$ nm, in excellent agreement with experiment.

A more fruitful approach would involve using the Mössbauer resonance data on Au^{197} to derive information about the core excitation. Since the theory is still essentially phenomenological, further understanding of this excitation mode will depend considerably on new measurements. With certain assumptions, we can derive from the excited-state magnetic moment and the chemical shifts in Au^{197} the deformation parameter and magnetic moment of the excited core. The assumptions are reasonable but may easily be wrong, and the values derived thereby should be regarded with appropriate skepticism.

If we assume that Eq. (2) is the correct relationship among all the factors which contribute to the excited-state moment, and that g_p is unchanged for the odd $d_{3/2}$ proton from the ground state, it follows from Eq. (2) and the experimental value of $\mu_{1/2}$ that

$$g_c=+0.42\pm0.04\,. \tag{3}$$

A detailed interpretation of isomeric chemical shifts for Au^{197} in several metallic lattices has been made elsewhere.[31] With some assumptions of a chemical nature that are too involved to repeat here, a value

$$\delta R/R_s=(3\pm1)\times10^{-4} \tag{4}$$

may be derived for the nuclear factor. This is somewhat smaller than the value quoted in Ref. 31, in which a relativity correction factor was omitted. Here R_s is the average nuclear radius (7.0 F in the case of Au^{197}). This quantity $\delta R/R_s$ is the "directly measurable" nuclear factor in isomeric chemical shift experiments. Under the assumptions of constant nuclear charge density and equal nuclear volumes in the two isomeric states, an estimate of the difference between the nuclear deformations of the two states may be made. Wilets, Hill, and Ford[32] first calculated explicitly the optical isotope shifts associated with nuclear deformation. Their results were extended to optical isomeric shifts by Lardinois.[33] Barrett and Shirley[34] adapted the relations to treat isomeric chemical shifts in Mössbauer spectra. They obtained the approximate expression

$$\Delta E=(2\pi/5)Ze^2[3/(2\rho+1)]R_s{}^2\Delta[\textstyle\sum\psi(0)^2]$$
$$\times\Delta\{\alpha^2[1+(2/21)(2\rho+3)+\cdots]\}\,. \tag{5}$$

Here ρ is the relativistic electron parameter $(1-a^2Z^2)^{1/2}$, where a is the fine structure constant, the sum is over atomic electrons within the nucleus, the first Δ represents the difference taken between the source and absorber, the second Δ means the difference between isomeric states, and α is a deformation parameter. The right-hand side of (5) should be multiplied by a relativity correction which is about 6.8 for gold.[35] The nuclear surface is approximated by an ellipsoid having the equation $R(\theta)=R_s[1+\alpha P_2(\cos\theta)]$. Here θ is the polar angle from the symmetry axis of the ellipsoid.

By comparison of Eq. (5) with observed isomeric shifts, a value of

$$0.0004<\Delta\alpha^2<0.0008 \tag{6}$$

may be derived[31] for Au^{197}, with $\alpha_1>\alpha_0$. At this point we must estimate α_0 in order to evaluate α_1, the excited-core deformation. To do this rigorously, we would have to assign to the ground-state core the correct fraction of ground-state deformation (as measured by the known quadrupole moment of $+0.60(6)$ b[26]). Of course this would require a rather complete knowledge of the nuclear structure of the ground state, which is unavailable. We shall essentially ignore the contribution of the odd proton, on the grounds that a single shell-model hole in a $d_{3/2}$ proton shell would produce a much smaller quadrupole moment ($\sim$0.1 b), and estimate α_0 for the whole nucleus from the quadrupole moment. The relationship between the measured quadrupole moment and α is (to first order in α)

$$\alpha=\tfrac{5}{6}(Q/ZR_s{}^2)[(I+1/I)][(2I+3)/(2I-1)]\,. \tag{7}$$

This result is derived by combining Eqs. (3.16) and (72.24) of Ref. 36 and noting that $\alpha=(2/3)\epsilon$, where ϵ

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is a deformation parameter. We thus obtain $\alpha_0 = +0.065$ (7). Combining this with Eq. (6) we find $\alpha_1 = +0.069$ (13). This corresponds to a value of $+0.10$ for the more customary deformation parameter ϵ, and thus a substantial nuclear deformation.

This analysis must be regarded as semiquantitative at best. In view of the assumptions involved it is appropriate to say that the calculated deformation "is consistent with," but not that it "follows directly from," the data. If the assumptions are wrong, some new type of shift in charge distributions would have to be taking place between the two states. If this should be the case, the derived numerical value of ϵ would be meaningless. This parameter was derived, however, simply to assign the observed shifts a position on a familiar "collective effects" scale.

VII. CONDUCTION-ELECTRON POLARIZATION

The signs and magnitudes of the internal fields derived in Sec. IV strongly support the idea that they arise through polarization of the 6*s* "conduction" electrons of Au dissolved in ferromagnetic 3*d* transition metals by exchange interaction with electrons on the transition-metal atoms. This conclusion follows from three types of evidence, discussed separately below:

(1) The hyperfine fields are all negative. This is expected from the conduction-electron polarization mechanism if, for example, the 6*s* electrons of gold are polarized by a positive exchange interaction with the spin-polarized outer electrons on the neighboring magnetic atoms, provided that these outer electrons have a negative spin density relative to the 3*d* electron spins. Freeman and Watson[37] have done exchange polarized Hartree-Fock calculations for Fe atoms which indicate that the outer-electron spin density is negative. It is well known that this behavior is generally expected for transition metals because the 4*s* electron eigenstate with *positive* spin should contract radially through an attractive interaction with the 3*d* shell, allowing the radially larger negative spin 4*s* eigenstate to dominate the outer portion of the transition-metal atom.

Our measurements do not, of course, establish which electrons on Fe directly polarize the 6*s* gold electron. The above mechanism is the principal one which has been discussed in the literature, but exchange polarization with the core electrons and 3*d* electrons on the transition-metal atoms must surely contribute terms to the 6*s* Au electron polarization. Perhaps the best way to decide the relative importance of such effects is to study the pressure dependence of the internal field in these systems. The amount of overlap of the Au 6*s* electrons with transition-metal outer electrons should vary quite sensitively with sample volume. An indirect indication that this polarization mechanism is important is the large effect attributed to "magnetostriction" in Sec. V.

(2) The internal field magnitudes in Au are approximately proportional to the effective magnetic moments of the host metals (Fig. 5). Thus, irrespective of the polarization mechanism details, the experimental internal fields can be understood as being caused by one type of interaction which is proportional to, and thus probably caused (albeit indirectly) by the unpaired 3*d* electron moment on the transition atoms. The induced fields do not seem to be sensitive to the host crystal structure.

We note that while Roberts and Thomson found the internal fields at Au in Fe, Co, and Ni to be proportional, within experimental error, to the effective host magnetic moments,[18] we find a small deviation from linearity in Fig. 5. If this deviation is real there may be a competitive mechanism contributing to the induced field, thereby making the situation somewhat more complicated than indicated above. The simple linear relationship was not observed for the case of Sn dissolved in Fe, Co, and Ni,[16] and the internal field in Sn is probably caused by a more complicated set of competing interactions. Again, the internal fields at Cu atoms dissolved in Fe and Co (212.7 and 157.5, respectively),[15] are not exactly proportional to the host moments. In all three cases (Cu, Sn, Au), the ratio of magnitude of induced field to effective atomic magnetic moment of host is smaller for Co than for Fe hosts, and for Sn and Au the nickel data are also consistent with this trend. These observations may indicate the existence of a competing *positive* contribution to the induced hyperfine field of the impurity atom which is not proportional to the diamagnetic impurity atom's conduction-electron polarization. This contribution competes most effectively in Sn where the "conduction-electron" term is small, actually changing the sign of the resultant field for Sn in Ni, and least effectively in Au, where the "conduction-electron" term is very large.

(3) The magnitudes of the induced internal fields seem to follow the magnitudes of the hyperfine fields created in the free atoms by the outer (conduction) electrons.

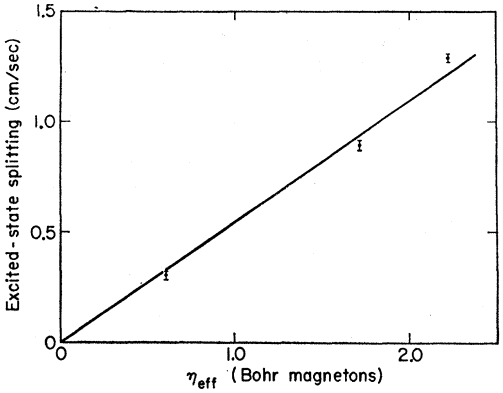

FIG. 5. Splitting of the 77-keV isomeric state in Au^{197} versus the atomic magnetic moment of the ferromagnetic host metal.

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Tin is an exception probably because of its complicated electronic structure and the complexity of the induced field, discussed above. The very large induced fields in Au and Re[17] dissolved in Fe are probably particularly significant, as both elements have 6s electrons with associated large fields. The internal field in atomic copper in the $4s^2S_{1/2}$ state is 1.3×10^6 G and that of atomic gold in the $6s^2S_{1/2}$ state is 21×10^6 G. These fields can be derived by using Eq. (15.5) in Ref. 36 and appropriate data from atomic spectroscopy.[38,39] Thus the internal fields of Cu and Au in Fe would correspond to 16% and 7% polarization of the conduction electrons, respectively. The internal field in atomic Ag in the $5s^2S_{1/2}$ state is 4.9×10^6 G.[40] It would be interesting to determine the induced field at Ag atoms dissolved in Fe, which should be ~400 kG by analogy with Cu and Au.

Notes added in proof. (a) Dr. A. de Shalit (private communication) has informed us that newer data on transition rates in Au^{197} would lower the core-excitation estimate of μ_{77} from +0.60 nm to about the experimental value of +0.37 nm. From calculations on the quasiparticle model, L. Kisslinger and R. A. Sorensen have also predicted a very low value (~0.12 nm) for this moment (private communication).

(b) The unusual low-field behavior of our samples was reversible. If this behavior is the result of spin orientation, a more significant zero-field splitting may be obtained by extrapolating back the high-field slopes. We acknowledge a discussion of this point with Dr. R. J. Elliott.

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Perturbation Theoretic Calculation of Polaron Mobility*

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The low-temperature drift mobility of the polaron is calculated in perturbation theory with the aid of the Kubo formula. The result is $\mu=\mu_0(1-\alpha/6)$, where μ_0 is the weak coupling mobility $\mu_0=(e/2\alpha\omega m)\exp(\hbar\omega/kT)$. A comparison is made with the perturbation expansion of various intermediate coupling mobility theories. The expansion of Osaka, $\mu=\mu_0(1-0.173\alpha+\cdots)$, agrees most closely with the exact perturbation expansion. It is concluded that the Osaka formula is probably the best in the intermediate coupling range $\alpha<6$. It is explicitly shown to lowest nontrivial order in α that various quasiparticle concepts are valid, viz., that $\mu=e\tau/m^*$, and that the electron density is a momentum integral over $f(E(\mathbf{p}))$.

I. INTRODUCTION

The drift mobility of a slow electron in the conduction band of a polar crystal has been the subject of much theoretical investigation.[1–9] There exist a large number of expressions for the low-temperature drift mobility, which unfortunately differ considerably in the experimentally interesting range[10,11] of coupling constant ($\alpha\sim3$). This spread of results is illustrated for several representative theories in Fig. 1. Notice that at $\alpha=3$, the results of Low and Pines differ from the results of Schultz by a factor of 6. Clearly it would be desirable to find out which of the various theories is most reliable. We attack the problem here by obtaining a perturbation expansion of the mobility in a power series in the coupling constant; we then compare the exact perturbation expansion with the power series expansion of the various intermediate coupling theories. This is done in the belief that the best intermediate coupling theory is likely to have a power series expansion which corresponds quite closely to the exact expansion.

Thus, the main body of this paper is concerned with finding the first nontrivial term in the expansion of the

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[11] Reference 6 summarizes experimental mobility data on the intermediate coupling materials AgCl and AgBr.