PHYSICAL REVIEW VOLUME 162, NUMBER 2 10 OCTOBER 1967

New Determination of the Nuclear Gyromagnetic Ratio γ of Co^{59}†

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(Received 25 April 1967)

The nuclear gyromagnetic ratio γ of Co^{59} has been redetermined from NMR studies of the intermetallic compounds CoSi and $CoSi_2$, yielding the new value $\gamma/2\pi = 1.0054 \pm 0.002$ kHz/G. These materials possess weak dia- and paramagnetism, respectively. The analysis consists of placing upper limits on the NMR shifts in these compounds by using measured values of susceptibilities and spin-lattice relaxation times T_1 and the well-known relations between shift and susceptibility contributions from orbital and spin-paramagnetic sources. Our findings are further supported by shifts observed for dilute cobalt in a number of transition-metal alloys. The new value of γ given above is larger by $\sim 0.9\%$ than the commonly accepted one of Freeman, Murray, and Richards that was obtained by extrapolation in their study of NMR shifts and optical splittings in cobaltic complexes. In view of this discrepancy, the theory of Van Vleck shifts in these complexes is reexamined in terms of a molecular orbital model of covalent mixing.

I. INTRODUCTION

It has been customary to assume that accurate values for nuclear magnetic moments may be obtained from precise gyromagnetic ratio measurements of the nuclei in question, when the atomic, or ionic, host is nominally nonmagnetic. For example, the nuclei of sodium or chlorine in a NaCl solution are thought to suffer only an extremely small core diamagnetism when placed in an external field, since the Na^+ and Cl^- ions consist of closed-shell configurations. The situation is considerably more complicated when the nuclei involved belong to transition metal ions.

Three cases need to be distinguished in discussing the problem of the nuclear moments of transition-metal ions: First, there are those elements for which the atomic ground state has fewer than three or four *d* electrons (e.g., Sc) and for which it is possible to make nonmagnetic closed-shell ions by forming a molecular complex with a "closed-shell" core (e.g., Sc_2O_3). Second, there are the elements in the middle of the 3*d*, 4*d*, and 5*d* long periods (e.g., Mn) for which the high valence states (e.g., Mn^{7+}), though nominally nonmagnetic are, in fact, not so.[1] The third case includes the atoms with almost filled *d* shells for which even pseudo-closed-shell ionic states are difficult to obtain (e.g., Fe, Co, and Ni). For this case, resort is often made to finding nonmagnetic ionic configurations in crystals. For example, in the configuration d^n, with n even, there is a domain where the electrostatic crystalline-field potential exceeds the Hund's rule energy. The ground state in this case has vanishing diagonal elements of S_z and L_z. However, the off-diagonal elements of **L** do not vanish and as a consequence, there is obtained the familiar temperature-independent high-frequency Van Vleck paramagnetism and related orbital paramagnetic shifts of the nuclear magnetic resonance (NMR). Since the magnitude of these shifts may be as much as 1% or more, it is imperative to account for their origin to an accuracy of 10% or better, if the *absolute* value of the nuclear moment is to be known to a precision of 0.1%, which is the requisite accuracy for the interpretation of Knight shifts in the related metals and alloys. Our particular interest in hyperfine field studies in the transition metals has led us to reexamine the existing work on the shifts of the Co^{59} NMR.

Cobalt is a particularly interesting case for several reasons. The Co^{59} NMR shift has been extensively studied[2] in a number of $Co^{3+}(3d^6)$ "low-spin" complexes and it was found that the shift varies as much as 1.3% from one complex to the next. A general interpretation of the shifts in terms of Van Vleck paramagnetism has been given by Griffith and Orgel[3] in which the shifts were shown to be related to the crystal-field splittings of the corresponding complexes. There followed a detailed NMR and associated optical work on many Co^{3+} complexes by Freeman, Murray, and Richards[4] (FMR). Using the theory of Griffith and Orgel[3] they were able to find, by extrapolation to infinite crystal-field splitting, the unshifted gyromagnetic ratio γ of Co^{59}. By a completely different experimental approach to be presented below, we find a value of γ that differs by about 1% from the FMR extrapolation, leading to greatly reduced measured shift values for the cobaltic complexes.

Our value of γ is based on Co^{59} NMR in the intermetallic compounds $CoSi_2$ and CoSi, which exhibit weak

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† Work supported in part by the National Science Foundation.

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[3] J. S. Griffith and L. E. Orgel, Trans. Faraday Soc. **53**, 601 (1957).

[4] R. Freeman, G. R. Murray, and R. E. Richards, Proc. Roy. Soc. (London) **242A**, 455 (1957).

paramagnetic[5] and diamagnetic[6] susceptibilities, respectively. In Sec. II, the shifts in these compounds are deduced from the orbital and spin-paramagnetic contributions to the susceptibilities, using the relationship between shift and susceptibility[7,8,9] that has been applied to a number of transition metals and intermetallic compounds. Additional information which correlates shifts with effective density of states at the Fermi energy $N(E_F)$ has been obtained by measuring the nuclear spin-lattice relaxation time T_1 for $CoSi_2$ and CoSi. These results, along with observed shifts for a number of cobalt alloys, form a coherent over-all picture which leads to the value of $\gamma(Co^{59})$ presented here.

Since our experimental results and their interpretation differ so markedly from the FMR work, we felt it necessary to reexamine the Griffith-Orgel model for the cobalt complexes in greater detail. This is done in Sec. III. We emphasize that the molecular orbital (MO) model we employ is at best a very rough approximation for complexes as covalent as $Co(CN)_6{}^{3-}$ and is incapable of giving quantitative results. We aspire instead to the more modest objective of determining whether a qualitative explanation for the reduced shifts in these complexes might be found with this approach.

In Sec. III we identify three distinct mechanisms by which covalency modifies the free-ion value of the orbital shift σ_{VV} in a given complex. We summarize these briefly here.

First, there is the well-known phenomenon of orbital reduction, wherein the matrix elements of the orbital angular-momentum operator **L** are diminished by contamination of the ionic *d* orbitals with any admixture of ligand orbital. (Although this was considered by Griffith and Orgel, we believe they underestimated its importance.) As will be seen in Sec. III this effect may be divided into two parts: (a) normalization reduction, which is simply the dilution of the *d* orbitals by the ligand admixture, and (b) a cancellation (or enhancement) of the *d*-orbital matrix element by the admixture and overlap terms. Effect (a) alone leads to proportional changes in σ_{VV} and χ_{VV}, preserving the ratio σ_{VV}/χ_{VV}. Effect (b), however, affects σ_{VV} and χ_{VV} unequally, owing to the strong radial dependence of the orbital hyperfine interaction $H_{hf}{}^{(orb)} \sim \mathbf{L}/r^3$. The full consequences of the latter effect will be discussed in Sec. III.

Finally, we note that $\sigma_{VV} \propto \langle 1/r^3 \rangle$, where the expectation value is taken for the 3*d* orbitals in the *complex*. For high covalency, one might expect this quantity to deviate considerably from the free-ion values and, in fact, to be reduced. This is analogous to the effective reduction of hyperfine fields for atoms in a metal.

II. NEW EXPERIMENTAL DETERMINATION OF γ OF Co^{59}

In this section we report on and analyze the NMR shift, relaxation time, and susceptibility data for $CoSi_2$ and CoSi to obtain the nuclear gyromagnetic ratio γ of Co^{59}. Some additional measurements on the Co^{59} shifts for dilute Co impurities in other host metals are presented and are in support of the results obtained from the $CoSi_2$ and CoSi studies.

The resonance frequency data were taken with a conventional crossed-coil NMR spectrometer using a supplementary proton gaussmeter and frequency counter for precise field calibrations. Measurements of the spin-lattice relaxation time T_1 were made using pulsed, spin-echo techniques. The specimens were prepared from stoichiometric amounts of semiconductor grade Si and Co (99.99%) by induction melting in recrystallized Al_2O_3 crucibles under an argon atmosphere. The ingots were subsequently zone refined. X-ray measurements and metallographic observations were made to insure a homogeneous single phase. Finally they were crushed and sieved to be suitable for NMR spectroscopy. No attempt was made to anneal these brittle intermetallic compounds either before or after crushing.

Necessary supplementary data on the magnitude and temperature dependence of the susceptibility of selected samples of $CoSi_2$ and CoSi were kindly provided by other workers at the Bell Telephone Laboratories.[10]

A. Interpretation of the NMR Shifts and Susceptibilities in $CoSi_2$ and CoSi

As a qualitative starting point, we remark that the compounds in question are metallic or semimetallic with regard to transport properties and general temperature independence of the susceptibility. Since the primary constituent element Co is a transition metal atom, we resort to the two-band (*s* and *d*) model interpretation of Knight shifts and susceptibilities that has been so useful in similar studies of the transition metals and certain transition-metal intermetallic compounds. In this tight-binding model the susceptibility χ is the sum of the separate contributions to the Pauli spin paramagnetism, $\chi_p{}^s$ and $\chi_p{}^d$, from *s* and *d* electrons, respectively, plus the orbital (Van Vleck) paramagnetism χ_{VV} of the incompletely filled degenerate

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[10] We wish to thank H. J. Williams and R. C. Sherwood of this laboratory for the use of unpublished χ-versus-T data for these materials.

bands. Thus,

$$\chi = \chi_{\rm dia} + \tfrac{2}{3}\chi_P{}^s + \chi_P{}^d + \chi_{\rm VV}, \qquad (1)$$

where $\chi_{\rm dia}$ is the sum of the diamagnetism of the core electrons plus the electrons in the *filled* portion of the d bands. The Knight-shift counterpart of Eq. (1) is

$$K = K_s + K_d + K_{\rm VV} = \alpha_s \chi_P{}^s + \alpha_d \chi_P{}^d + \beta \chi_{\rm VV}, \qquad (2)$$

where the quantities α_s and α_d are proportional to the hyperfine fields per spin for the s-contact and d-core polarization hyperfine interactions, respectively. The constant of proportionality in both cases is 0.895×10^{-4}. The quantity β is related to the orbital hyperfine field and is given by $\beta = (2/A)\langle 1/r^3\rangle_{\rm met}$, where A is Avogadro's number and the subscript on the expectation value of $1/r^3$ for the d electrons in question indicates that the average should be taken over the radial wave function in the metal.

We proceed to estimate the quantities α_s, α_d, and β for cobalt:

α_s: We know $H_{\rm hf}{}^{(s)} = (16\pi/3)\mu_B\langle\psi_{4s}(0)^2\rangle_{\rm met}$ and it has been estimated[11] that for cobalt $\langle\psi_{4s}(0)^2\rangle_{\rm at} = 0.45\times10^{27}$ cm^{-3}. As is common, we assume that there is a reduction of amplitude of the s-wave function at the nucleus in a metal, i.e., $\langle\psi_{4s}(0)^2\rangle_{\rm met} = \xi_s\langle\psi_{4s}(0)^2\rangle_{\rm at}$ with $\xi_s \sim 0.7$. It follows that $\langle\psi_{4s}(0)^2\rangle_{\rm met} \cong 0.32\times10^{27}$ cm^{-3}, $H_{\rm hf}{}^{(s)} = 2.92\times10^6$ Oe, and $\alpha_s = 262$.

α_d: The core polarization field $H_{\rm hf}{}^{(d)}$ may be obtained from the large body of empirical data that now exists for the $3d$ ions in nonmetallic crystals where it is found, for example, that for Mn^{2+}:d^5 that $H_{\rm hf}{}^{(d)} \cong -2.3\times10^5$ Oe. For the present case we assume that the large and negative hyperfine field in ferromagnetic cobalt arises entirely from core polarization. With this approach we find $H_{\rm hf}{}^{(d)} = -2.6\times10^5$ Oe and $\alpha_d = -23.3$. We will adopt these values.

β: Hartree-Fock calculations for $\langle 1/r^3\rangle_{\rm at}$ exist[12] for the d configurations corresponding to Co^{0+} and Co^{2+}. We assume that a value for $\langle 1/r^3\rangle_{\rm at}$ for Co^{1+} would be more appropriate to the metal and find, by interpolation, that $\langle 1/r^3\rangle_{\rm at} = 5.4$ atomic units. Assuming the reduction of this quantity in the metal[13] to be such that $\langle 1/r^3\rangle_{\rm met} = \frac{3}{4}\langle 1/r^3\rangle_{\rm at}$, i.e., $\xi_{\rm VV} = 0.75$, we find $\beta = 95$.

Before utilizing these values to estimate the respective contributions to the Knight shifts in the two compounds, it should be remarked that the major uncertainties in the quantities finally derived do *not* arise from uncertainties in the hyperfine fields but rather in the division of the relative amount of d-spin and d-orbital paramagnetism. Furthermore, though there is little question that the latter quantities are to be associated with the cobalt atoms, question does arise as to whether there is, in fact, a sizable s-like contribution to χ from the silicon atoms. Here we proceed by estimating $\chi_P{}^s(\mathrm{Si})$ from the measured Si^{29} Knight shift. Further, the s-electron-state density *for the cobalt atoms alone* is inferred from the measured T_1. In this way an upper limit is set for $K_s(\mathrm{Co})$, which is all that is important for the argument to be presented below. With the above, we now consider the new shift and susceptibility data and their interpretation.

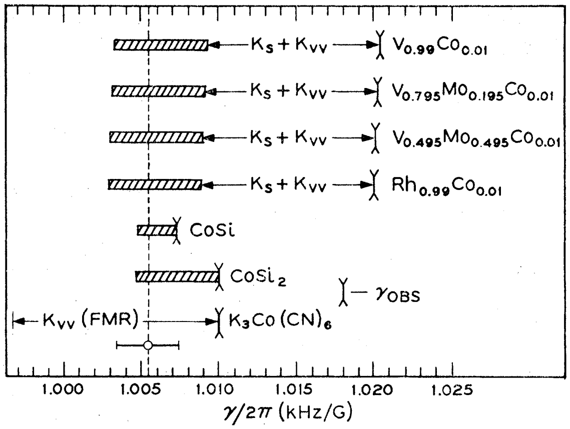

FIG. 1. Observed nuclear gyromagnetic ratios (γ) and estimated shifts for Co^{59} in $\mathrm{CoSi_2}$, CoSi, and a number of dilute cobalt alloys. Also shown for comparison is the observed γ for $\mathrm{Co(CN)_6}^{3-}$ and the corresponding shift estimate given by Freeman, Murray, and Richards. The unshifted value of $\gamma(\mathrm{Co}^{59})$ determined by the present work is shown as a vertical dashed line.

$\mathrm{CoSi_2}$: This intermetallic compound has the C1 ($\mathrm{CaF_2}$-type) structure in which both sites have cubic point symmetry. As a result a relatively strong Co^{59} NMR signal is observed whose linewidth ($\delta H \simeq 4$ Oe) presumably results from nuclear dipole-dipole interactions alone. The observed effective gyromagnetic ratio $\gamma_{\rm obs} = \nu_{\rm res}/H_0$ of Co^{59} in $\mathrm{CoSi_2}$ is shown in Fig. 1, along with $\gamma_{\rm obs}$ for $\mathrm{K_3Co(CN)_6}$, CoSi, and certain alloys. $\chi_{\rm obs}$ and $\gamma_{\rm obs}$ for $\mathrm{CoSi_2}$ were found to be essentially temperature-independent between helium and room temperatures, with $\chi_{\rm obs} = 34.6\times10^{-6}$ emu/mole. Note that $\gamma_{\rm obs}$ for $\mathrm{CoSi_2}$ is almost indistinguishable from that for $\mathrm{K_3Co(CN)_6}$. It is this complex that FMR found to have a positive shift of 1.4% in their interpretation of the Van Vleck paramagnetism of cobaltic complexes (here and throughout we ignore core diamagnetic shifts). Their corrected value of γ for Co^{59} is shown on the left side of Fig. 1 for comparison with the present data.

The shaded area to the left of $\gamma_{\rm obs}$ for $\mathrm{CoSi_2}$ shows the range of possible unshifted γ's for this substance. This range is derived as follows: The greatest positive shift (smallest γ) consistent with our data would result if (1) the d-spin contribution to $\chi_{\rm obs}$ were negligibly small and (2) the observed T_1 ($T_1T = 1.5$ sec °K) were due entirely to the s band. These suppositions are not in conflict since $\chi_{\rm VV}$ could be appreciable even with a vanishingly small $N_d(E_F)$.

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With these conditions imposed we can make the following estimates: (1) The observed value of T_1T provides an upper limit on K_s via use of the Korringa relation[14]; $K_s \leq 0.18\%$. Then from Eq. (2), $\chi_p^s(\mathrm{Co}) = 6.8 \times 10^{-6}$ emu/mole. (2) $\chi_p^s(\mathrm{Si})$ is estimated from the measured Si^{29} shift, $K_s(\mathrm{Si}) = 0.031\%$ by comparison with the observed shift, and (specific-heat) density of states for Al^{27} in Al. Using $K_s = \alpha_s \chi_p^s$, we have

$$\chi_p^s(\mathrm{Si}) = \chi_p^s(\mathrm{Al})[K_s(\mathrm{Si})\alpha_s(\mathrm{Al})/K_s(\mathrm{Al})\alpha_s(\mathrm{Si})]. \quad (3)$$

Knight[15] gives for the atomic hyperfine coupling constants, $a_s \propto \alpha\gamma_s$: $a_s(\mathrm{Al})/a_s(\mathrm{Si}) = 1.5$. Thus $\alpha_s(\mathrm{Al})/\alpha_s(\mathrm{Si}) = H_{\mathrm{hf}}^s(\mathrm{Al})/H_{\mathrm{hf}}^s(\mathrm{Si}) = 1.15$, which is quite reasonable since these elements are neighbors in the periodic table. Using $K_s(\mathrm{Al}) = 0.162\%$ and $\chi_p^s(\mathrm{Al}) = 20.10^{-6}$ derived from $\gamma_{\mathrm{sp.\,ht.}}(\mathrm{Al}) = 3.48 \times 10^{-4}$ cal/mole °K², we find from Eq. (3) that $\chi_p^s(\mathrm{Si}) = 4.4 \times 10^{-6}$ emu/mole. So small is this value that an uncertainty of 100% would still be unimportant for the present purposes. (3) χ_{dia} is calculated assuming $\chi_{\mathrm{dia}} = \chi_{\mathrm{dia}}(\mathrm{Co}^+) + 2\chi_{\mathrm{dia}}(\mathrm{Si})$. Using the Hartree-Fock value[12] $\langle r^2 \rangle = 1.70$ a.u. for the $3d$ electrons in Co^+, we find that $\chi_{\mathrm{dia}}(\mathrm{Co}^+) = -Ze^2\langle r^2 \rangle/6\ mc^2 = -10.8 \times 10^{-6}$ emu/mole with $Z=8$. With the measured value $\chi_{\mathrm{dia}}(\mathrm{Si}) = -3.9 \times 10^{-6}$ emu/mole for pure Si, a value of $\chi_{\mathrm{dia}}(\mathrm{total}) = -18.6 \times 10^{-6}$ emu/mole is obtained. (4) Finally, it is found that $\chi_{\mathrm{VV}} = \chi_{\mathrm{obs}} - \frac{2}{3}\chi_p^s(\mathrm{total}) - \chi_{\mathrm{dia}}(\mathrm{total}) = 42.8 \times 10^{-6}$ emu/mole and $K_{\mathrm{VV}} = 0.41\%$. Thus, the greatest *positive* shift consistent with these measurements is $K_{\mathrm{VV}} + K_s = 0.59\%$. This corresponds to the left-hand boundary of the shaded region for CoSi_2 in Fig. 1.

To the extent that the d-electron magnetism is of spin origin, the total shift in CoSi_2 will be less positive than given above and may even become slightly negative. A rough estimate of the least positive shift consistent with our data would make it nearly zero. A precise calculation is not in order, since it will be seen below that γ_{obs} for CoSi provides the upper bound (see Fig. 1) for the unshifted γ, and γ_{obs} for CoSi corresponds to a sizeable positive shift for CoSi_2. The shaded area shown for CoSi_2 in Fig. 1 gives the total range of unshifted γ values. Even so, it is to be noted that the smallest value $\gamma/2\pi = 1.0041$ kHz/G is 0.8% higher than the corrected value given by FMR.

CoSi: The most attractive feature of this transition metal compound is that it possesses temperature-independent *diamagnetism* with $\chi_{\mathrm{obs}} = -30 \times 10^{-6}$ emu/mole.[5,6] Since it is manifestly unreasonable to presume all d subbands to be filled, it would appear that the diamagnetism is a consequence of band structure—large diamagnetism occurs frequently for metals with almost filled (empty) zones. Assuming the band gaps not to be prohibitively large ($\Delta < 0.3$ eV) we must suppose there to be a finite orbital paramagnetism (involving the admixture of *empty* states above the gap into *filled* states below the gap by the combined action of **L** and the external field) which is masked by an anomalously large Landau diamagnetism due to the low-mass electrons (holes) in regions of **k** space near the Brillouin zone boundaries. This conjecture is supported by measured χ values for alloys of the form $\mathrm{CoSi}_{1-x}\mathrm{Al}_x$. In Fig. 2, it is seen that replacing a small amount of Si with Al (having one fewer electrons) quenches the diamagnetism. Abrupt changes in the thermoelectricity with the composition of such alloys have also been observed. We shall use the alloy results to estimate χ_{VV} for CoSi.

Our procedure then to obtain reasonable values for the Knight shift parameters in CoSi is as follows: (1) determine the effective gyromagnetic ratio γ_{obs}, (2) use the T_1 result to place upper limits on K_s and K_d, (3) determine χ_{VV}, and (4) determine the bounds on the "true" $\gamma(\mathrm{Co}^{59})$ from the limits imposed by the values of K_s, K_d, and K_{VV}.

(1) Although the space-group symmetry of CoSi is cubic (B-20 FeSi-type structure), neither the cobalt nor the silicon site have cubic point symmetry—the symmetry of both sites being 3. For the Co^{59} nuclei, with $I = \frac{7}{2}\hbar$, both an axially symmetric nuclear electric quadrupole interaction and anisotropic Knight shift become allowed by this low symmetry and, indeed, both are observed. The net effect of these combined interactions somewhat complicates the analysis of the observed spectra. The detailed observations, which were made as a function of field and temperature, and their interpretation are confined to Appendix A along with the definition of the parameters given in Table I. For our present purposes we are only interested in the

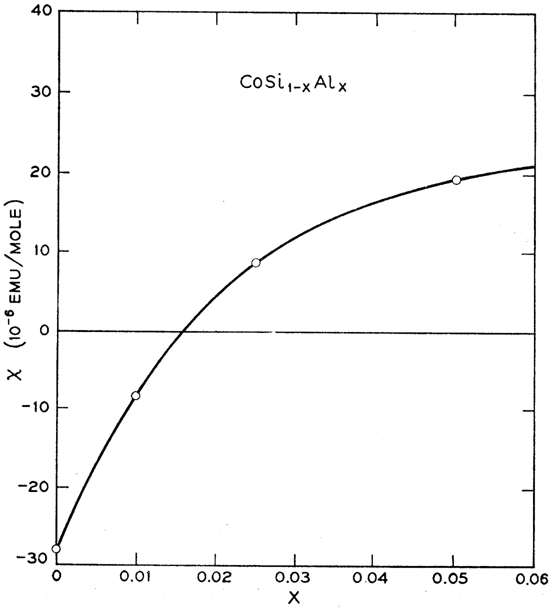

FIG. 2. Measured susceptibility of the compounds $\mathrm{CoSi}_{1-x}\mathrm{Al}_x$ plotted as a function of x, the fractional aluminum content.

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[14] J. Korringa, Physica 16, 601 (1950).

[15] W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2.

TABLE I. Quadrupolar and anisotropic Knight-shift parameters and effective gyromagnetic ratio for CoSi.

	γ_{obs}	b	ν_Q	$a=K_{\mathrm{ax}}$
293°K	1.0072 kHz/G±0.0003	$(2.31\pm0.12)\times10^5$ kHz^2	0.498 MHz	$-(3.8\pm0.8)\times10^{-4}$
20.4°K	1.0076 kHz/G±0.0003	$(1.95\pm0.1)\times10^5$ kHz^2	0.457 MHz	···

effective γ which from Table I appears to be temperature-independent within experimental error.

(2) Measurements of T_1 were made on several different CoSi samples as a function of temperature. In addition to the scattering of itinerant electrons (which gives a contribution to T_1 proportional to T^{-1}) the relaxation rate measurements showed important quadrupolar contributions to T_1, particularly at higher temperatures. The details of this are given in Appendix B along with a discussion of the model theory necessary to abstract effective values of K_s and K_d. However, for our present purposes, the essential result is that the intrinsic itinerant electron contribution limits $T_1T\geq46$ sec °K. If we were to assume that all of the latter resulted from s electrons, it would make $K_s\leq0.03\%$, and correspondingly if d electrons were responsible then $|K_d|\leq0.02\%$. Clearly then, even if we were to allow for errors as large as 100%, the relaxation measurements indicate the complete lack of importance of *spin* contributions to the Co^{59} Knight shift in CoSi. It might be mentioned here, as an aside, that the electronic specific heat[16] of CoSi ($C_v=\gamma T$) yields a value of $\gamma=2.8\times10^{-4}$ cal/mole °K which is substantial. The relevance of this to the T_1 observations is also discussed in Appendix B.

(3) We need only to estimate an upper limit for K_{VV} to obtain the maximum range of positive Co shift $K_{\mathrm{VV}}+K_s$ in CoSi. To do this we utilize the susceptibility data for the system $\mathrm{CoSi}_{1-x}\mathrm{Al}_x$ shown in Fig. 2. The increase in χ with aluminum concentration is attributed mainly to a quenching of the anomalous diamagnetism—we neglect the changes in $\chi_p{}^s$ and χ_{VV} that would result from a slight change in the position of the Fermi level, since both these quantities are insensitive to changes in E_F. On the other hand, $\chi_p{}^d$ being rather small in pure CoSi might well increase appreciably with added aluminum. Were this the case we would be required to reduce the upper limit χ_{VV} which we deduce from the alloy measurements. Assuming then that the "quenching" process is complete for $\mathrm{CoSi}_{0.95}\mathrm{Al}_{0.05}$ we find $\chi_{\mathrm{VV}}\cong25\times10^{-6}$ emu/mole since χ_{dia} and $\chi_p{}^s$ are approximately equal in magnitude and opposite in sign. Such a value for χ_{VV} implies a value of $K_{\mathrm{VV}}\cong0.22\%$ and therefore a *maximum positive shift* for CoSi of $K_{\mathrm{VV}}+K_s\simeq0.25\%$. This amount is shown as the shaded region for CoSi in Fig. 1; it should not be taken too seriously. In fact, we shall depend on CoSi_2 to limit the minimum possible values of $\gamma(\mathrm{Co}^{59})$ consistent with the data. Our interpretation of the alloy data does, however, indicate the possibility of a 0.25% positive shift in CoSi. It is also consistent with the above interpretation that there was no measurable shift of the Co^{59} resonance in $\mathrm{CoSi}_{0.975}\mathrm{Al}_{0.025}$ from that in pure CoSi.

Thus the results for CoSi_2 and CoSi bracket the possible values of γ on the left and right, respectively: $1.0041\leq\gamma/2\pi\leq1.0072$ kHz/G. Without further knowledge about the magnetism in these and other cobalt compounds, it is not possible to specify the γ of Co^{59} any more accurately than the limits given. As it is not likely that the d-electron magnetism in these compounds arises entirely from either spin or orbital origins, we specify the best value of γ as

$$\gamma/2\pi=1.0054\ \text{kHz/G},\ \pm0.2\%. \tag{4}$$

The generous error limit given allows for possible error in the parameters used to estimate K_{VV}.

The value of γ in Eq. (4) is seen to differ from the FMR value ($\gamma/2\pi=0.9963$) by about 0.9%. *There is no way within the present framework to stretch our interpretation of the silicides to make up this discrepancy.* The origin of the implied error in the treatment of the Co^{3+} complexes given by FMR and by Griffith and Orgel is discussed in the next section.

B. Co^{59} Shifts in Dilute Co Alloys

Finally, the reasonable nature of our value of γ is established by means of a rough interpretation of Co shifts in several transition metal alloys in which cobalt appears as a dilute ($\leq1\%$) nonmagnetic impurity. Values of γ_{obs} for Co^{59} in each of these alloys are shown in Fig. 1. Most surprising, at first, is that the Co shifts are so nearly alike although as we now show this is exactly what one could expect on the basis of a simple impurity model.

Let us treat K_s, K_d, and K_{VV} for these alloys in turn.

(1) K_s: We know K_s for any Co impurity must be less than the Knight shift of Cu in copper since in this latter case the s-hyperfine interaction is larger and it is generally assumed that there is one electron/atom in the s-conduction band. Since $K(\mathrm{Cu})=0.23\%$ we take $K_s\leq0.2\%$.

(2) K_d: Since we are concerned with finding an upper limit on the positive shift in all of the alloys the most generous assumption concerning K_d is that it is identically zero. In any case, its neglect is reasonable since $|\alpha_d|/\beta\simeq0.25$ for Co and we expect $\chi_{\mathrm{VV}}\geq\chi_p{}^d$.

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[16] V. Jaccarino, G. K. Wertheim, J. H. Wernick, L. R. Walker, and F. Arajs, Phys. Rev. **160**, 476 (1967).

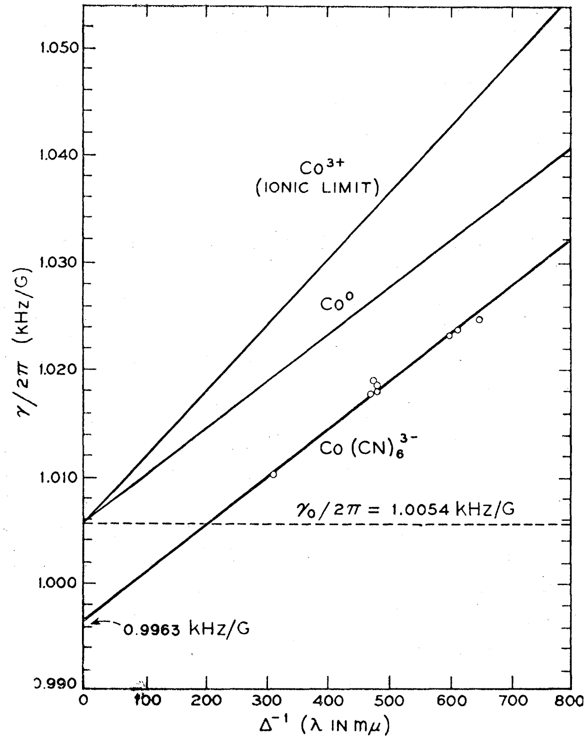

FIG. 3. Observed gyromagnetic ratios of Co^{59} for a number of octahedral cobaltic complexes plotted as a function of Δ^{-1}, where Δ is the energy splitting between the ground state and the lowest-lying state of T_{1g} symmetry (data taken from Ref. 4) The extrapolated value of $\gamma(Co^{59})$ given by FMR is shown at bottom left.

(3) K_{VV}: In order to estimate K_{VV} we adopt a simple model for χ_{VV} in a d-band metal, namely, that, aside from details of the symmetries and structure of the band, one expects[8] $\chi_{VV} \propto N_0 N_u$, where N_0 and N_u are the number of occupied and unoccupied d states on the Co atom. Moreover, since shielding of impurities in d-band metals is expected to take place on the atom itself, the value of $N_0 N_u$ is expected to remain roughly constant for Co atoms in any metallic d-band environment. Hence, the constancy of shift for the alloys in Fig. 1 is to be associated with the constancy of χ_{VV} for the impurity. With this simple picture we may estimate $\chi_{VV}(Co)$ from the very large value $\chi_{VV} = 211$ emu/mole found for vanadium metal as follows:

$$\chi_{VV}(Co) = (N_0 N_u)_{Co} / (N_0 N_u)_V \times \chi_{VV}(V). \tag{5}$$

With one s electron per atom we find $(N_0 N_u)_{Co} = 16$, $(N_0 N_u)_V = 24$, and $\chi_{VV}(Co) = 141 \times 10^{-6}$ emu/mole. Then with $\beta = 95$, one finds $K_{VV} = \beta \chi_{VV} = 1.34\%$ for each alloy. The total shift $K_s + K_{VV}$ is shown in Fig. 1 for each alloy with a shaded region corresponding to $\pm 0.25\ K_{VV}$ to allow for some reasonable error. The value of γ given in Eq. (4) is seen to lie well within the shaded region in each case. It is felt that the value of χ_{VV} necessary to reconcile the alloy shifts with the value of γ given by FMR is unreasonably large, since this would require $\chi_{VV}(Co) > \chi_{VV}(V)$. Further, any shift contribution from K_d would move the shaded regions to the right, requiring still greater values of χ_{VV} to account for the γ value determined by FMR.

In summary, it is concluded that the Co resonances in all of the systems examined here indicate a significantly higher value of γ than the extrapolated value given by FMR, and that the actual value of γ lies within the limits given in Eq. (4).

III. VAN VLECK SHIFTS AND SUSCEPTIBILITIES IN OCTAHEDRAL COBALTIC COMPLEXES.

A. The NMR Shift Data

In this section we reexamine the (positive) Co^{59} NMR shifts σ_{VV} and magnetic susceptibilities χ_{VV} of the octahedral $3d^6$ cobaltic complexes. We reiterate that σ_{VV} and χ_{VV} arise from second-order perturbation terms involving matrix elements of $\mathbf{L}$ and $\mathbf{L}/r^3$ between the A_{1g} ground state and T_{1g} excited states of a given complex. To calculate these quantities, Griffith and Orgel[3] adopted a simple "ionic" model in which only the lowest-lying T_{1g} excited state was considered to be important, and both ground- and excited-state wave functions were assumed to consist of pure ionic $3d$ orbitals. The splitting $\Delta = E(T_{1g}) - E(A_{1g})$ results from the interaction of the cobalt $3d$ electrons with the octahedral potential due to the ligands.

On this basis one expects $\sigma_{VV}, \chi_{VV} \propto \Delta^{-1}$,[17] and in Fig. 3 the observed nuclear gyromagnetic ratios for a variety of cobalt complexes are plotted against measured values of Δ^{-1}. These data are taken from the work of FMR, who gave the straight-line ($\sigma_{VV} = B_0/\Delta$) interpretation shown. The slope B_0 is in reasonable agreement with theory, and the intercept at $\Delta^{-1} = 0$ gives an unshifted γ value of 0.9963 kHz/G as shown in Fig. 1. Viewed in this way, shifts of these complexes would range from 1.4 to 2.8%.

However, we reinterpret these shifts with the new gyromagnetic ratio for Co^{59} (denoted γ_0) derived in Sec. II.[18] This is shown as a horizontal baseline in

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[17] The Griffith-Orgel model of σ_{VV} and χ_{VV} also implies the same relationship $\sigma_{VV} = \beta \chi_{VV}$ where $\beta = (2/A)\langle 1/r^3 \rangle$, which is so useful in treating the transition metals. One might ask why this relation cannot be used here to estimate σ_{VV} from measured susceptibilities. There are two reasons for this. First, measured χ values for these complexes contain a large and indeterminate amount of diamagnetism which obscures the χ_{VV} contribution. Second, we shall see in Part B below that the simple relation stated above breaks down for large covalency. Thus, one must be extremely cautious in relating σ_{VV} to χ_{VV} for such systems even if the latter quantity can be accurately determined.

[18] Recently, observed Co^{59} gyromagnetic ratios for a number of organo-cobalt compounds have been reported [E. A. C. Lucken, K. Noack, and D. F. Willians, J. Chem. Soc. (London) A, **1**, 148 (1967)]. These compounds all possess *smaller* positive shifts than that of $Co(CN)_6^{3-}$ (the smallest of the octahedral cobaltic series), yet have positive shifts with respect to the new value of $\gamma(Co^{59})$ reported here. Although the authors measure and interpret their shift data with the FMR moment value, we feel that these data are not in conflict with the present work. In particular for the case of the carbonyls and derivatives, where the cobalt atomic $3d$ shell is nominally closed, it is thought that our γ value gives much more realistic shift estimates (0.1 to 0.2%).

Fig. 3. As a result, the shifts are all reduced by $\sim 0.9\%$, and they no longer obey a simple linear dependence on Δ^{-1} as was predicted by the ionic model. The discrepancy with the ionic model is most clearly seen by plotting $\gamma(\Delta)=\gamma_0[1+\sigma_{VV}(\Delta)]$, taking for $\sigma_{VV}(\Delta)$ the expression given by Griffith and Orgel,[3]

$$\sigma_{VV}=\frac{32\mu_B^2\langle 1/r^3\rangle_{3d}}{\Delta}. \qquad (6)$$

This is shown as the uppermost line in Fig. 3, where we have used $\langle 1/r^3\rangle_{3d}=6.7$ a.u. given by Freeman and Watson[12] for the pure $3d$ orbitals of Co^{3+}. The obvious lack of agreement with such a theory suggests that the effects of covalency are more important here than was previously realized. Our major task then in this section will be to give a *qualitative* explanation of the shift behavior in terms of covalent mixing of the atomic orbitals.

The effects of covalency in transition-metal complexes are well known. First, augmentation of the d orbitals with ligand p functions reduces the matrix element values of $\mathbf{L}$ (orbital reduction). In EPR studies this alters orbital g shifts and leads to diminished spin-orbit coupling parameters. This effect would also diminish the Van Vleck shifts and susceptibilities considered here.

In addition, for strong covalency the octahedral ligand potential will seriously distort the d orbitals and consequently change $\langle 1/r^3\rangle_{3d}$. Concerning the latter effect very little reliable information seems to be available. We proceed here by observing that, qualitatively, covalency will tend to make the ionic potential look more like that of the neutral atom, in accord with Pauling's charge neutrality principle of covalent bonding, and thus reduce $\langle 1/r^3\rangle$. For example, molecular orbital calculations[19] for $Co(NH_3)_6{}^{3+}$ have been interpreted to show that only 0.3 units of charge reside on the cobalt atom, instead of the nominal 3 units. We might guess, then, that the Hartree-Fock[12] value for Co^{0+} $[\langle 1/r^3\rangle=4.8$ a.u.$]$ would be more appropriate for σ_{VV} estimates in these complexes. The corresponding expression for $\gamma(\Delta)$ from Eq. (6) is plotted in Fig. 3, giving a somewhat closer approximation to the data. For the purposes of our discussion we shall adopt the Co^0 curve in Fig. 3 as a reference curve, attributing the remaining discrepancy to an orbital reduction factor $k'^2(\sigma)$. Such an estimate will be adequate for the qualitative discussion to follow.

It was noted by Griffith and Orgel[3] that orbital reduction effects may diminish σ_{VV} and χ_{VV} in the cobaltic complexes, but only small changes were expected to occur $[1-k'^2(\sigma)\ll 1]$. From Fig. 3 we find, to the contrary, that $k'^2(\sigma)\sim 0.4$ for $Co(CN)_6{}^{3-}$. It was further suggested by Griffith[20] that one might account for covalency here by inserting a constant orbital reduction parameter k'^2 into the right-hand side of Eq. (5) $[\sigma_{VV}=32\mu_B^2k'^2\langle 1/r^3\rangle/\Delta]$. This procedure would change the slope, but not the $\Delta^{-1}=0$ intercept of the line, and therefore we must consider a possible variation of k'^2 with Δ. One might expect k'^2 to diminish with increasing Δ, giving the greatest reduction of σ_{VV} for $Co(CN)_6{}^{3-}$ and causing the intercept of a straight line through the data to fall below γ_0, as is observed. This interpretation would explain the failure of FMR's extrapolation procedure to yield the correct Co^{59} moment. It appears, in fact, somewhat accidental that the data fell on a straight line. The implied correlation of large energy splitting Δ with small values of k'^2 is is not unreasonable, since in some sense both are a measure of covalency.

The rather large reduction effects found here are not entirely without precedent. Spin-orbit coupling parameters λ have been found to be reduced by 36% for $K_3Fe(CN)_6$ by Bleaney and O'Brien[21] and by more than 50% for Fe^{2+}:ZnF_2 by Tinkham.[22] λ is closely analogous to σ_{VV}, since they are both second-order effects having a strong radial dependence.

B. Molecular Orbital Model

We now develop our interpretation of the orbital reduction effect further using the molecular orbital model. This is accomplished by constructing MOLCAO wave functions for the ground- and excited-states and obtaining expressions for χ_{VV} and σ_{VV} in terms of covalent admixture and overlap parameters. To our knowledge such a calculation has not been discussed in the literature in connection with Van Vleck paramagnetism and NMR shift. Our procedure is similar to Stevens' work[23] on ground-state orbital reduction and follows closely the work of Tinkham[22] on spin-orbit coupling in the system Fe^{2+}:ZnF_2.

We adopt a simplified model, allowing admixture only of a p_π and p_σ orbital of the proper symmetry in the ground- and excited-states, respectively. Anticipating that a large amount of covalency will be required to obtain the estimated $k'^2(\sigma)\sim 0.4$ for $Co(CN)_6{}^{3-}$, we emphasize the inherent limitations of the MOLCAO picture for such a case and expect only qualitatively correct results. Accordingly, we take no account of the "back-donation" effects to antibonding ligand π orbitals that may be important in the cyanides.[24]

In the high-field approximation the ground- and excited-state configurations are treated as pure $t_{2g}{}^6$ and $t_{2g}{}^5e_g$ configurations, respectively. Griffith and Orgel[3] have pointed out that deviation from this picture can only increase σ_{VV} and χ_{VV}, making the discrepancy

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[20] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, Cambridge, England, 1964), Chap. 12.

[21] B. Bleaney and M. C. M. O'Brien, Proc. Phys. Soc. (London) **569**, 1216 (1956).

[22] M. Tinkham, Proc. Roy. Soc. (London) **A236**, 549 (1956).

[23] K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 542 (1953).

[24] R. G. Shulman and S. Sugano, J. Chem. Phys. **42**, 39 (1965).

between theory and experiment here even greater. Within this framework the shift and susceptibility may be expressed as

$$\sigma_{\mathrm{VV}}=(2e^2/m^2c^2\Delta)\langle\psi_g\mid l_z\mid\psi_e\rangle\langle\psi_e\mid l_z/r^3\mid\psi_g\rangle \quad (7)$$

and

$$\chi_{\mathrm{VV}}=(e^2A/m^2c^2\Delta)\mid\langle\psi_g\mid l_z\mid\psi_e\rangle\mid^2, \quad (8)$$

where ψ_g and ψ_e are ground- and excited-state single-electron orbitals with the symmetry properties of xy and x^2-y^2, respectively. A is Avogadro's number. Contributions from l_x and l_y are identical by symmetry and are included in Eqs. (7) and (8) by a multiplicative factor.

The molecular-orbital approach consists in approximating ψ_g and ψ_e as follows:

$$\psi_g=N_\pi[\varphi_{xy}-\lambda_\pi\chi_\pi] \quad (9)$$

and

$$\psi_e=N_\sigma[\varphi_{x^2-y^2}-\lambda_\sigma\chi_\sigma], \quad (10)$$

where φ's are the pure metal ion d orbitals and χ_π and χ_σ are linear combinations of ligand p orbitals that possess the requisite symmetries. Normalization of ψ_g and ψ_e requires

$$N_\pi^{-2}=[1-4\lambda_\pi S_\pi+\lambda_\pi^2],$$

$$N_\sigma^{-2}=[1-4\lambda_\sigma S_\sigma+\lambda_\sigma^2], \quad (11)$$

where $S_{\pi,\sigma}$ are defined to be positive overlap integrals between a single ligand p orbital and the appropriate d orbital. Substitution of Eqs. (9)-(11) into Eq. (8) gives

$$\chi_{\mathrm{VV}}=(16A\mu_B^2/\Delta)\times\{N_\pi^2N_\sigma^2[1-2(\lambda_\pi S_\pi+\lambda_\sigma S_\sigma)-\lambda_\pi\lambda_\sigma/2]^2\}, \quad (12)$$

where we identify the quantity in braces to be $k'^2(\chi)$ and note that this quantity is positive definite. For small values of the parameters λ_π, λ_σ, S_π, and S_σ, the quantity $k'^2(\chi)$ reduces to

$$k'^2(\chi)\cong 1-\frac{(\lambda_\pi^2+\lambda_\sigma^2+\lambda_\pi\lambda_\sigma)}{[1-4(\lambda_\pi S_\pi+\lambda_\sigma S_\sigma)+\lambda_\pi^2+\lambda_\sigma^2]}. \quad (13)$$

Equation (13) shows that slight covalency always leads to a reduction of χ_{VV} and is analogous to the expression for ground-state orbital reduction.[23]

Similar substitutions into Eq. (7) give

$$\sigma_{\mathrm{VV}}=\frac{32\mu_B^2}{\Delta}N_\pi^2N_\sigma^2[1-2(\lambda_\pi S_\pi+\lambda_\sigma S_\sigma)-\lambda_\pi\lambda_\sigma/2]^2$$

$$\times\left\{\frac{\langle\varphi_{xy}\mid l_z/r^3\mid\varphi_{x^2-y^2}\rangle}{\langle\varphi_{xy}\mid l_z\mid\varphi_{x^2-y^2}\rangle}-2\lambda_\pi S_\pi\frac{\langle\varphi_{x^2-y^2}\mid l_z/r^3\mid\chi_\pi\rangle}{\langle\varphi_{x^2-y^2}\mid l_z\mid\chi_\pi\rangle}\right.$$

$$\left.-2\lambda_\sigma S_\sigma\frac{\langle\varphi_{xy}\mid l_z/r^3\mid\chi_\sigma\rangle}{\langle\varphi_{xy}\mid l_z\mid\chi_\sigma\rangle}-\frac{\lambda_\pi\lambda_\sigma}{2}\frac{\langle\chi_\pi\mid l_z/r^3\mid\chi_\sigma\rangle}{\langle\chi_\pi\mid l_z\mid\chi_\sigma\rangle}\right\}. \quad (14)$$

The first term in the curly brackets is just $\langle 1/r^3\rangle_{3d}$, but the other terms are not so simply evaluated since they involve two-center integrals. We can represent the expression in curly brackets schematically as

$$\{\langle 1/r^3\rangle_{3d}-2\lambda_\pi S_\pi\langle 1/r^3\rangle_{d\pi}-2\lambda_\sigma S_\sigma\langle 1/r^3\rangle_{d\sigma}-\lambda_\pi\lambda_\sigma/2\langle 1/r^3\rangle_{\pi\sigma}\},$$

where $\langle 1/r^3\rangle_{d\pi}$ and $\langle 1/r^3\rangle_{d\sigma}$ are of the order of $d^{-3/2}a^{-3/2}$ and $\langle 1/r^3\rangle_{\pi\sigma}$ is of the order of d^{-3}, where d is the ion-ligand interatomic distance and $a=[\langle 1/r^3\rangle_{3d}]^{-1/3}$. Since a typical value of d is several atomic units we expect $\langle 1/r^3\rangle_{d\pi}$, $\langle 1/r^3\rangle_{d\sigma}$, and $\langle 1/r^3\rangle_{d\pi}\ll\langle 1/r^3\rangle_{3d}$; thus, we neglect all terms in { } except the first one and find

$$\sigma_{\mathrm{VV}}=\frac{32\mu_B^2\langle 1/r^3\rangle_{3d}}{\Delta}k'^2(\sigma),$$

where

$$k'^2(\sigma)=N_\pi^2N_\sigma^2[1-2(\lambda_\pi S_\pi+\lambda_\sigma S_\sigma)-\lambda_\pi\lambda_\sigma/2]. \quad (15)$$

The factors $k'^2(\sigma)$ and $k'^2(\chi)$ incorporate two distinct effects. First, the normalization reduction factors $N_\pi^2N_\sigma^2$ result purely from the admixture process used to form an extended molecular orbital. Second, there is a cancellation of p-d overlap matrix elements of **L** with the ionic d-orbital term embodied in the factor $[1-2(\lambda_\pi S_\pi+\lambda_\sigma S_\sigma)-\lambda_\pi\lambda_\sigma/2]$. This factor appears in the first power for $k'^2(\sigma)$ and squared for $k'^2(\chi)$, implying a significant difference between these quantities. For this reason and because of the indeterminacy of $\langle 1/r^3\rangle$ one must be extremely cautious in relating observed shifts and susceptibilities. We apply these results, Eqs. (12) and (15), to the case of $\mathrm{Co(CN)_6}^{3-}$ by first estimating λ_π, S_π, and S_σ and then plotting the resulting

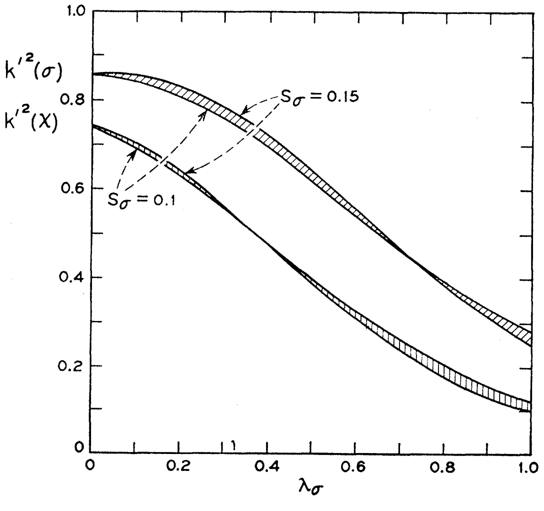

FIG. 4. Calculated values of the orbital reduction factors $k'^2(\sigma)$ and $k'^2(\chi)$ for shift and susceptibility, respectively, plotted as a function of λ_σ for $\lambda_\pi=0.5$, $S_\pi=0.1$, and for two values of S_σ, 0.1 and 0.15.

expressions as a function of λ_σ. Note that λ_π, $\lambda_\sigma > 0$ for these antibonding orbitals (neglecting back-donation). Now, using an estimate of $S_\pi \sim 0.1$ from previous calculations[25] we may obtain an approximate value of λ_π from the measured ground-state orbital reduction factor $k = 0.87$ for the closely similar low-spin complex $Fe(CN)_6{}^{3-}$. Stevens' expression[23] $k = 1 - \lambda_\pi{}^2/[2(1-4\lambda_\pi S_\pi + \lambda_\pi{}^2)]$ then yields a value of $\lambda_\pi \cong 0.52$. One might expect $S_\sigma > S_\pi$; we therefore plot $k'^2(\chi)$ and $k'^2(\sigma)$ versus λ_σ in Fig. 4 with $\lambda_\pi = 0.5$ and $S_\pi = 0.1$ for two values of S_σ, 0.10 and 0.15, as shown.

The plots show a remarkable insensitivity to S_σ for the two values chosen. The large difference between $k'^2(\sigma)$ and $k'^2(\chi)$ implies a breakdown of the simple relationship $\sigma_{VV} = \beta\chi_{VV}$ with $\beta = (2/A)\langle 1/r^3 \rangle$ as mentioned earlier. It is seen that a value of $\lambda_\sigma \sim 0.8$ is required to obtain the estimated value $k'^2(\sigma) \sim 0.4$ for $Co(CN)_6{}^{3-}$.

This is a very large admixture parameter, and one must question the validity of the MOLCAO model for such a case. It does compare favorably, however, with the value $\lambda_\sigma = 0.65$ found by Yamatera[26] in a calculation of the d splitting 10 Dq for the somewhat less covalent complex $Co(NH_3)_6{}^{3+}$.

Let us turn briefly to the implication of Fig. 4 for χ_{VV}. With $\lambda_\sigma = 0.8$ we find that χ_{VV} is reduced to only 20% of its ionic value, namely to a value of the order of $\chi_{obs} = 32 \times 10^{-6}$ emu/mole. This seems unreasonable because it makes no allowance for diamagnetism. In this connection, however, we make the following two observations: (1) The expression for χ_{VV} [Eq. (14)] makes no allowance for coupling with other excited states of the complex. Such coupling may generate contributions to χ_{VV} comparable to Eq. (14) and thus allow for a certain amount of diamagnetism $\chi_{dia} = \chi_{obs} - \chi_{VV}$. Moreover, contributions to χ_{VV} from other excited states would tend to be associated with small values of $\langle 1/r^3 \rangle$ and therefore of shift because of their radial diffuseness (e.g., $4d$ ionic and charge-transfer states). (2) Further, Ballhausen and Asmussen[27] have discussed the diamagnetism of Co^{3+} and Rh^{3+} complexes and found $|\chi_{dia}|$ to be correlated with the spectrochemical series and to have the smallest values for the cyanides. Our results suggest that $|\chi_{dia}|$ may even by smaller than these authors estimated, approaching a value still closer to the closed-shell limit that they quote ($\chi_{dia} = -15 \times 10^{-6}$ emu/mole for $Zn(en)_3{}^{+2}$ owing to the covalency of the ground state.

Again, we emphasize the schematic and therefore qualitative nature of our model. Even if the MOLCAO approximation were a good one for such covalent systems, we recognize that important features have been omitted for simplicity, and the values chosen for many of the parameters are but reasonable guesses. Our results, however, are suggestive of the following consistent picture of the behavior of σ_{VV} and χ in these complexes: (1) The major contribution to σ_{VV} comes from the lowest-lying (d-like) T_{1g} state and is greatly reduced by covalency. (2) The contribution to χ_{VV} from the above state is also severely reduced, and there are appreciable contributions from other states. (3) The diamagnestism is somewhat smaller than that found by Ballhausen and Asmussen[27] using an ionic model to estimate χ_{VV}. (4) The effects of covalency diminish in importance as Δ decreases.

ACKNOWLEDGMENTS

The authors would like to thank Dr. J. A. Seitchik for his early contribution to the NMR studies reported here, and D. Dovsi for experimental assistance.

APPENDIX A: ANALYSIS OF Co^{59} NMR SPECTRUM IN CoSi

As mentioned above the Co^{59} nuclear spins in CoSi are subjected to both an axial electric quadrupole tensor interaction and an anisotropic Knight shift. For the present work these are effects to be measured and "corrected for" in order to find γ_{obs}, i.e., the position the NMR line would have in their absence. We give here only a brief discussion of the procedure used to analyze the associated NMR spectra and appropriate references to the literature for a more extensive treatment.

For applied fields H_0 that are large compared with ν_Q/γ, where $\nu_Q = 3e^2Qq/2hI(2I-1)$ is a measure of the quadrupole coupling, the NMR spectrum of $Co^{59}(I=\frac{7}{2})$ in powdered CoSi consists of an intense central $(m=\frac{1}{2}) \leftrightarrows (m'=-\frac{1}{2})$ transition flanked by six weaker, uniformly spaced satellites corresponding to transitions between higher m values.[28] All seven lines were clearly observable in the present investigation.

Of major interest here is the central transition with its inherently better signal-to-noise ratio because of its narrower linewidth. The absorption derivative of this transition is itself split into two peaks by the combined effects of anisotropic Knight shift and second-order quadrupolar interaction. These peaks correspond to the extrema of the distribution of $(\frac{1}{2} \leftrightarrows -\frac{1}{2})$ transition frequencies in a powdered specimen, and are displaced from the Larmor frequency ν_L by the amounts[29]

$$\Delta\nu_+ = b/\nu_L - a\nu_L$$

and

$$\Delta\nu_- = -(16b/9\nu_L) + \tfrac{2}{3}a\nu_L - (a^2\nu_L{}^3/4b). \qquad \text{(A1)}$$

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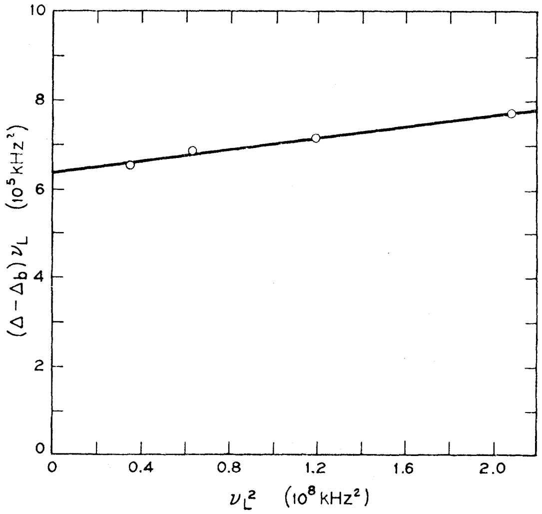

FIG. 5. Measured splitting Δ of the central $(\frac{1}{2}\leftrightarrows\frac{1}{2})$ NMR transition of Co^{59} in CoSi, for a number of resonance frequencies, plotted so as to determine the anisotropic Knight shift and second-order quadrupolar parameters (slope and intercept, respectively).

Here $b=\nu_Q{}^2[I(I+1)-\frac{3}{4}]/16$ is the second-order quadrupolar splitting parameter and $a=K_{\text{ax}}/(1+K_{\text{iso}})$ is the anisotropic Knight-shift coefficient, where the total shift is given by $K(\theta)=K_{\text{iso}}+K_{\text{ax}}(3\cos^2\theta-1)$, θ being the angle between the crystalline symmetry axis and the applied field.

The procedure used to find $\gamma_{\text{obs}}=\nu_L/H_0$ is first to measure a and b and then insert these values in Eqs. (A1) to obtain the precise value of ν_L in a given field. The parameters a and b are obtained from observation of the variation of the splitting Δ as a function of applied field, where $\Delta=\Delta\nu_+-\Delta\nu_-+\Delta_b=(25/9)b/\nu_L-(5/3)a\nu_L+\Delta_b$, and Δ_b is a contribution from dipolar broadening and field modulation effects. If a plot $(\Delta-\Delta_b)\nu_L=(25b/9)-(5/3)a\nu_L{}^2$ as a function of $\nu_L{}^2$ is made, there is found a straight line of slope $-(5/3)a$ and intercept $25b/9$ (neglecting the third term in $\Delta\nu_-$ as a very small correction). Such a plot for CoSi at room temperature is shown in Fig. 5, giving $b=(2.31\pm0.12)\times10^5$ kHz² and $a=-(3.8\pm0.8)\times10^{-4}$. For the purpose of this plot we have estimated $\Delta_b\cong6$ kHz (a modulation of 4-Oe peak-to-peak was used) and determined γ_{obs} to better than 1% from the data with the smallest splitting $\Delta(\nu_L=14.5$ MHz, $\Delta=59.3$ kHz). The uncertainties in a and b arise mainly from our imprecise knowledge of Δ_b. (An independent determination of b was made by measuring the splittings of the satellite lines which are proportional to ν_Q. There has been obtained a value of $\nu_Q=0.495$ MHz, corresponding to $b=2.30\times10^5$ kHz², in excellent agreement with the value given above.)

Finally, γ_{obs} is obtained from the best data ($\nu_L=14.5$ MHz) using Eqs. (A1). The splitting Δ_b is divided equally between the two peaks in finding ν_L. The principal result, $\gamma_{\text{obs}}=1.0072$ kHz/G, is thought to be accurate to ±0.03%.

The temperature independence of γ_{obs} was verified by means of a measurement at 20.4°K. Here the satellite splittings were found to be ~10% smaller with $\nu_Q=0.457$ MHz. Using this value to calculate b and the room-temperature value of a, Eqs. (A1) were used to find $\gamma_{\text{obs}}=1.0076$ kHz/G. The difference of 0.04% between this and the room-temperature result is within the combined experimental error. The results given in this appendix are summarized in Table I.

It is of some interest to note that the measured value of $a=K_{\text{ax}}$ is too large to be accounted for in terms of p- or d-electron dipolar interactions, even with the drastic assumption that only one of the degenerate orbitals from these bands is populated at the Fermi surface. It is most likely that the anisotropy in the observed shift originates with an anisotropy in K_{VV}. Although the over-all cubic symmetry of the crystal requires χ_{VV} to be isotropic, the local noncubic symmetry allows for each of the sites in the unit cell to have an orbital g tensor with unequal diagonal elements. From the latter there is obtained a possible source of anisotropy to K_{VV}.

APPENDIX B: MEASUREMENTS OF T_1 FOR CoSi

Here we discuss and interpret T_1 measurements that were made on a number of specimens of CoSi in order to gain further information about the various sources of shift present. Pulse techniques were employed for these measurements, using both free-induction signals and spin echoes with virtually identical results.

T_1T is given for two specimens at several temperatures in Table II. Specimen No. 1 gave the longest T_1 values of those tried and specimen No. 2 was typical of the others. We tabulate T_1T rather than T_1 since we are attempting to identify the conduction-electron contribution to this process for which one would expect T_1T to be constant. It is seen from Table II that T_1T behaves in a rather complicated way indicating the presence of nonintrinsic processes which vary from specimen to specimen. Nevertheless, the following general conclusions may be drawn from these data:

(1) At room temperature there is a dominant

TABLE II. Values T_1T of the Co^{59} NMR at 10 MHz for two specimens.

T(°K)	T_1T (sec°K) (No. 1)	T_1T (sec °K) (No. 2)
293	7.35	6.83
77	46.	...
20	42.4	3.7
4.2	34.4	3.1

(intrinsic) quadrupolar T_1 process. This process varies faster than T^2 in this region ($T \ll \Theta_{\mathrm{Debye}}$) and is relatively unimportant at 77°K or below.

(2) The data at 77°K and below show a large variation between specimens and typically decreasing values of T_1T with decreasing temperature. The origin of this behavior is not completely understood. It is clear from specimen No. 1, however, that the intrinsic conduction-electron T_1 process is very weak ($T_1T \gg 1$). For this reason we suggest that "relaxation centers" provided by fast-relaxing Co^{59} nuclei in nonstoichiometric regions or defect sites of the crystal are contributing significantly to the bulk T_1 of specimen No. 2 via spin diffusion. For example, the low-temperature values of T_1T for specimen No. 2 cannot represent an intrinsic conduction-electron process, since this would result in an *even smaller* T_1T at room temperature contrary to observation. (One might expect a cross-relaxation process, such as we propose, to yield increasing T_1T values at higher temperatures because of the temperature-independent spin-diffusion "bottleneck." Thus the "relaxation centers" may obey a $T_1 \propto T^{-1}$ law, but the bulk nuclei cannot follow at high temperatures because of poor thermal contact. It is also consistent with this interpretation that T_1T for specimen No. 2 at 20°K exhibited a field dependence, increasing by ~33% on going from 7 to 12 kG. This would result from a relative shift between the bulk and "fast-relaxing" nuclei, effectively weakening the cross relaxation between these systems as they are split further apart by the applied field.)

(3) By this reasoning we conclude then that specimen No. 1 gives the closest approximation to the intrinsic relaxation times, and that $(T_1T)_{\mathrm{intrinsic}}$ cannot be smaller than the largest value measured. Thus we find $(T_1T)_{\mathrm{intrinsic}} \geq 46$ sec °K. We use this lower limit on T_1T to derive upper limits for the s-spin and d-spin shift contributions.

Upper limits for K_s and K_d may be estimated by attributing the entire relaxation rate first to the s-band and then to the d band. For the s-band Korringa's relation[14] gives $K_s < 0.03\%$ for $T_1T \geq 46$ sec °K, or $\chi_p^s \leq 1.1 \times 10^{-6}$ emu/mole. This is not, therefore, an important source of shift.

To assess the d-electron contribution to T_1 we use the theory of T_1 in transition metals.[13] In a two-band (s and d) model, the d-band contributes to $1/T_1$ via both the core-polarization and orbital hyperfine fields. We utilize the rate expressions [Eqs. (30a), (30b), and (30c) of Ref. 13] by substituting the hyperfine field values given in Sec. II and averaging over the range $0.2 \leq f \leq 1$, where f is the fractional Γ_5 character of the d band at the Fermi surface. Setting this expression for T_1T equal to 46 sec °K gives for the d-band state density $\eta_d \leq 9 \times 10^{10}$ states/erg-atom. From this we obtain $\chi_p^d \leq 9.2 \times 10^{-6}$ emu/mole, and from Eq. (2) above $|K_d| \leq 0.02\%$, where K_d is, of course, negative. Although this is admittedly a crude procedure, errors as large as 100% would not affect our conclusion that *K_d is also essentially negligible for* CoSi.

It is interesting to note that CoSi has been found to have an electronic specific heat comparable to that of many s-p band metals,[16] $\gamma = 2.8 \times 10^{-4}$ cal/mole °K², corresponding to a spin susceptibility $\chi_p^s + \chi_p^d = 16 \times 10^{-6}$ emu/mole. In view of this it seems paradoxical that the Co^{59} T_1 is so much weaker than that of, say, copper ($T_1T \sim 1$ sec °K). Without further knowledge of the band structure of this compound, we can only guess that a good fraction of the observed γ results from the s band of the silicon atoms and that the effective cobalt s-like density of states at the Fermi surface is rather small.