

Nuclear Spin-Lattice Relaxation in Cadmium and Tin*

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Pulsed nuclear-magnetic-resonance measurements of the spin-lattice relaxation time T_1 in Cd^{113} and Sn^{119} from 77 to 820°K are reported. An enhancement of the Korringa product $T_1TK_{\text{iso}}^2$ that is constant with temperature but different in the solid and liquid states is observed. For Cd^{113} , the difference between the liquid and solid enhancement is significant and can be related to a core-polarization or orbital contribution to the isotropic Knight shift K_{iso} . In solid Cd^{113} , the sum of these two contributions to K_{iso} is about -9% as large as the contribution from the contact hyperfine interaction and that fraction is independent of temperature. In liquid Cd^{113} and solid and liquid Sn^{119} , the sum of these contributions is probably small.

I. INTRODUCTION

THE nuclear magnetic resonance in Cd shows very unusual temperature dependences of the isotropic and anisotropic Knight shift, K_{iso} and K_{an} .¹⁻⁵ Both these unusual temperature dependences have now been explained⁶ in terms of the effect of the lattice vibrations on the band structure of Cd without invoking contributions from either core polarization K_{op} or orbital paramagnetism K_o . In this paper, we report measurement of the temperature dependence of the nuclear spin-lattice relaxation time, T_1 , which can be related to the observed value of K_{iso} and yield estimates of the magnitude of the sum of K_{op} and K_o . The behavior of the Korringa product $T_1TK_{\text{iso}}^2$ will be examined for Cd^{113} and compared with the behavior in Sn^{119} over the temperature range of 77-820°K. In both cases, we will conclude that the sum of the contributions K_{op} and K_o are less than 10% of the shift caused by the contact hyperfine interaction. This result justifies the theoretical calculation⁶ which neglected these contributions. Experimental details can be found in an Appendix.

II. THEORETICAL BACKGROUND

A. Isotropic Knight Shift

In metals, the contact hyperfine interaction gives rise to the contact Knight shift K_s ,^{7,8} from electrons with s character in their wave functions, and, therefore, is spherically symmetric. The K_s contribution to K_{iso} is always positive. The contact interaction can be in-

directly responsible for another contribution K_{op} to the isotropic Knight shift by means of the mechanism of core polarization; K_{op} can be either positive or negative. In metals in which there is considerable p or d character in the wave function, $K_s + K_{\text{op}}$ can be substantially different from K_s alone. The contribution of core polarization has not been calculated for either Cd or Sn, but as an indication of the size K_{op} can attain,⁹ in Al it is found that $K_{\text{op}} \approx -0.08K_s$. The orbital hyperfine interaction results in a contribution K_o to K_{iso} via an orbital paramagnetism. A reliable value of K_o is difficult to obtain, but estimates show that it could give a substantial contribution to K_{iso} in both Cd and Sn. Thus, there can be several contributions to K_{iso} ,

$$K_{\text{iso}} = K_s + K_{\text{op}} + K_o. \quad (1)$$

In the absence of a calculation for K_{op} and with no experimental method of separating the three contributions, this expression can be condensed to $K_{\text{iso}} = K_s + K'$.

B. Spin-Lattice Relaxation Time

For a noninteracting electron gas the simple Korringa relation should hold,^{8,10}

$$T_1TK_s^2 = (\hbar/4\pi k_B)(\gamma_s/\gamma_n)^2 \equiv S. \quad (2)$$

Note that the observed value of K_{iso} may not be the appropriate value for use in the Korringa relation, as may be seen from Eq. (1). Experimentally, it is observed that the product $T_1TK_{\text{iso}}^2$ is larger than S . This enhancement occurs because of electron exchange enhancement of both K_s and $1/T_1$.¹¹⁻¹⁵ The Korringa relation takes the new form¹⁵

$$T_1TK_s^2 = SK(\alpha)^{-1}, \quad (3)$$

where $K(\alpha)^{-1}$ expresses the enhancement; theoretically, $K(\alpha) \leq 1.0$, and values of $K(\alpha)$ near 0.75 are ex-

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¹ E. F. W. Seymour and G. A. Styles, Phys. Letters **10**, 269 (1964).

² F. Borsa and R. G. Barnes, J. Phys. Chem. Solids **27**, 567 (1966).

³ S. N. Sharma and D. Ll. Williams, *Colloque Ampere XIV* (North-Holland Publishing Co., Amsterdam, 1967), p. 480.

⁴ H. Schone, Phys. Rev. Letters **13**, 12 (1964).

⁵ R. G. Goodrich and S. A. Khan (to be published).

⁶ R. V. Kasowski and L. M. Falicov, Phys. Rev. Letters **22**, 1001 (1969).

⁷ W. D. Knight, *Solid State Physics* (Academic Press Inc., New York, 1956), Vol. II, p. 93.

⁸ C. P. Slichter, *Principles of Magnetic Resonance* (Harper & Row Publishers, Inc., New York, 1963).

⁹ W. M. Shyu, T. P. Das, and G. D. Gaspari, Phys. Rev. **152**, 270 (1966).

¹⁰ J. Korringa, Physica **16**, 601 (1950).

¹¹ D. Pines, *Solid State Physics* (Academic Press Inc., New York, 1955), Vol. I, p. 367.

¹² S. D. Silverstein, Phys. Rev. **128**, 631 (1962).

¹³ S. D. Silverstein, Phys. Rev. **130**, 912 (1963).

¹⁴ T. Moriya, J. Phys. Soc. Japan **18**, 516 (1963).

¹⁵ A. Narath and H. T. Weaver, Phys. Rev. **175**, 373 (1968).

pected.^{12,13} The value $K(\alpha)=0.75\pm 0.10$ is consistent¹⁶ with experiment for several nontransition liquid metals. The electron-phonon interaction has no effect upon T_1 .¹⁷

Besides the contact hyperfine interaction, there are other interactions which can influence the relaxation rate: spin-dipolar and orbital terms in the hyperfine Hamiltonian, core polarization, and in noncubic environments for metals with nuclear spin $\geq \frac{1}{2}$, an electric quadrupole contribution. Both Cd¹¹³ and Sn¹¹⁹ have nuclear spin $\frac{1}{2}$, so they can exhibit no quadrupolar contribution. Estimates show that the spin-dipolar and orbital contributions¹⁸ to the relaxation are negligible in Cd¹¹³ and Sn¹¹⁹. There can be core-polarization contribution to the relaxation rate,¹⁹

$$1/T_1 = (1/T_1)_s + (1/T_1)_{ep}, \quad (4)$$

where the s refers to the direct-contact hyperfine contribution. For core polarization induced by p character in the conduction-electron wave function, the Korringa-like relation also holds,¹⁹

$$(T_1)_{ep}TK_{ep}^2 = 3S. \quad (5)$$

Even if $|K_{ep}|$ is as large as $\frac{1}{10}K_s$, the core-polarization contribution to $1/T_1$ is negligible. This value of $|K_{ep}|$ will later prove to be a reasonable upper bound for Cd and Sn. Therefore, the situation in Cd and Sn is particularly favorable,

$$1/T_1 = (1/T_1)_s, \quad (6)$$

$$K_{iso} = K_s + K'. \quad (7)$$

We must be careful to note that any temperature dependence of the product of the observed quantities $T_1TK_{iso}^2$ can be ascribed to *either* a temperature-dependent fraction K'/K_s , or to a temperature dependence of the true enhancement factor $K(\alpha)$. Both these possibilities will be considered for Cd and Sn.

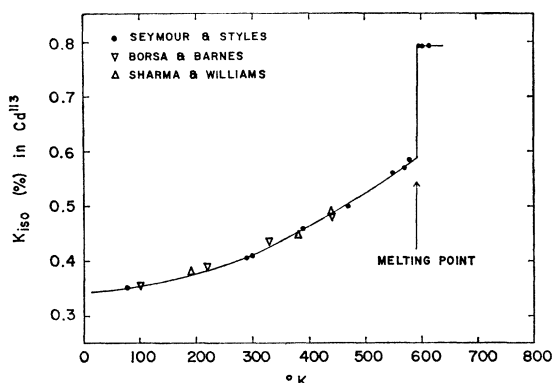


FIG. 1. K_{iso} versus temperature in Cd¹¹³ from other work. Notice the large discontinuity at the melting point.

¹⁶ F. A. Rossini, thesis, University of California, Berkeley, 1968 (unpublished); Phys. Rev. **178**, 641 (1969).

¹⁷ A. E. Prange and L. P. Kadanoff, Phys. Rev. **134**, A556 (1964).

¹⁸ Y. Obata, J. Phys. Soc. Japan **18**, 1020 (1963).

¹⁹ Y. Yafet and V. Jaccarino, Phys. Rev. **133**, A1630 (1964).

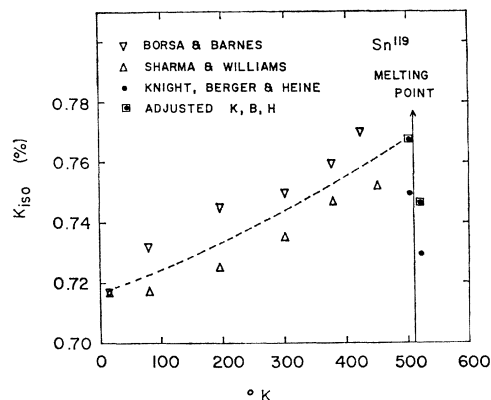


FIG. 2. K_{iso} versus temperature in Sn¹¹⁹ from other work. Notice the adjustment made of the data of Knight, Berger, and Heine to achieve agreement of the absolute value of K_{iso} , while preserving the measured change in K_{iso} at the melting point.

III. EXPERIMENTAL BACKGROUND

A. Knight Shift

Early experiments²⁰ on Cd showed that the value of K_{iso} in both the magnetic isotopes Cd¹¹¹ and Cd¹¹³ is the same. Subsequent experiments have examined only Cd¹¹³. The large temperature dependence of K_{iso} is shown in Fig. 1. Unlike most other metals,²¹ cadmium has the distinction of exhibiting a large abrupt change in Knight shift at the melting point.¹ However, in the liquid, Cd behaves like other liquid metals, showing only slight temperature dependence,²²

$$dK_{iso}/dT = K_{iso}(T_m)(0.55 \pm 0.15) \times 10^{-4}/^\circ\text{K}.$$

By contrast with Cd, the behavior of the NMR in Sn is not unusual. The behavior of K_{iso} is shown in Fig. 2; note that K_{iso} is nearly constant at the melting point.²¹ In the liquid, K_{iso} has only a slight temperature dependence,²²

$$dK_{iso}/dT = K_{iso}(T_m)(0.15 \pm 0.06) \times 10^{-4}/^\circ\text{K}.$$

B. Spin-Lattice Relaxation

Before the present work, no direct (i.e., pulsed) measurement of T_1 had been reported in Cd¹¹³. There had been one measurement of T_1 by the cw saturation method at room temperature²⁰ which yielded $T_1 = 500 \mu\text{sec}$ which is about $\frac{1}{2}$ the prediction of the unenhanced Korringa relation. This implied that other substantial relaxation mechanisms were present. It now seems likely that this low value of T_1 can be ascribed to experimental error from the indirectness of the saturation method and not to other significant relaxation mechanisms. Since this experimental work

²⁰ Y. Masuda, J. Phys. Soc. Japan **12**, 523 (1957); **13**, 597 (1968).

²¹ W. D. Knight, A. G. Berger, and V. Heine, Ann. Phys. (N. Y.) **8**, 173 (1959).

²² E. F. W. Seymour and G. A. Styles (private communication).

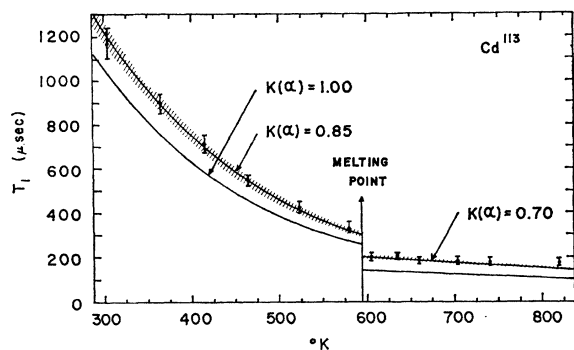


FIG. 3. T_1 versus temperature in Cd^{113} from this work. Solid line is the prediction of the unenhanced Korringa relation; solid line clothed in shading is the Korringa relation with an empirical fit for the enhancement. The cross-hatching represents uncertainty in the prediction arising from uncertainty and scatter in the measured values of K_{iso} . Notice the difference in enhancement in the solid and liquid states.

was completed, measurements of T_1 at 4.2 and 77°K were reported²³ which join smoothly onto the results reported here. Before the present work, there had been three measurements^{24–26} of T_1 in Sn^{119} at 77°K as shown in Fig. 4.

IV. EXPERIMENTAL RESULTS

The spin-lattice relaxation time T_1 has been measured at a resonance frequency of 9 MHz in samples of powdered Cd and Sn by conventional pulsed NMR techniques on equipment and samples described in the Appendix. The experimental results for Cd^{113} are shown in Fig. 3 for temperatures between 300 and 820°K. The results at 77°K are shown in Fig. 4. An attempt was made to take data in the supercooled region of Cd, but

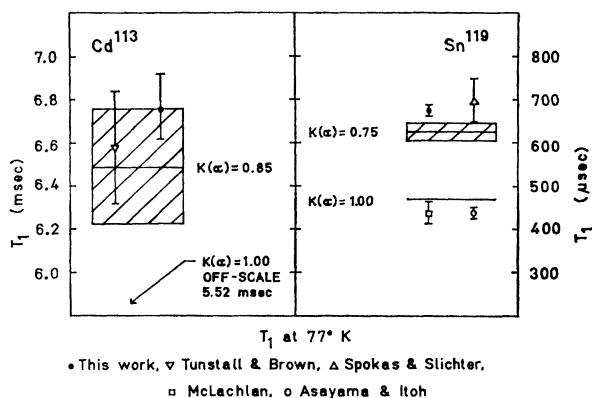


FIG. 4. T_1 at 77°K in Cd^{113} and Sn^{119} from this work compared to published values. Notice that for Sn^{119} the data of McLachlan, and Asayama and Itoh fall below the prediction of the unenhanced Korringa relation while the data of this work and Spokas and Slichter show an enhancement of about the magnitude expected.

²³ D. P. Tunstall and D. Brown, Phys. Letters 28A, 445 (1968).

²⁴ J. J. Spokas and C. P. Slichter, Phys. Rev. 113, 1462 (1959).

²⁵ K. Asayama and T. Itoh, J. Phys. Soc. Japan 17, 1065 (1962).

²⁶ L. A. McLachlan, Can. J. Phys. 46, 871 (1968).

the sample would not supercool by more than about 5°K, and even then the liquid signal steadily decreased while the solid signal steadily increased. It is possible to fit the observed T_1 with a single value of $K(\alpha)$ in the solid and another single value of $K(\alpha)$ in the liquid. This will be termed the “observed $K(\alpha)$ ” to distinguish it from the “true $K(\alpha)$ ” which arises from electron exchange only.

The data for Sn^{119} are shown in Figs. 4 and 5. The T_1 data at 77°K of this work agree with the Sn^{119} T_1 value of Spokas and Slichter²⁴ and severely disagree with McLachlan²⁶ and Asayama and Itoh.²⁵ No systematic errors in this work have been found that could account for the discrepancy. As a further check, T_1 was re-measured at 77°K in another sample from the same source and also in another sample of lesser purity and larger particle size. The T_1 values obtained for single determinations on these samples are 685 ± 21 and 654 ± 9 μsec compared to the average value from five runs of 676 ± 6 μsec obtained on the original sample. Because of the consistency of T_1 values obtained in this work, the data of McLachlan and Itoh are thought to be incorrect and are not considered further. As in Cd, the data can be fit with a single value of $K(\alpha)$ in liquid state. In the solid, above 300°K, a single value of $K(\alpha)$ suffices, but at 77°K, a lower value of $K(\alpha)$ is required. The value of $K(\alpha)$ in the liquid is more uncertain than in the solid owing to the adjustment²⁷ of the Knight-shift data in Sn^{119} . Therefore, the difference between the observed values of $K(\alpha)$ in solid and liquid Sn is thought to be insignificant, and $K(\alpha)$ will be considered to be the same in both states, at about 0.75. No attempt was made to obtain data in the supercooled region of Sn because T_1 in the liquid and solid were the same within experimental error.

V. DISCUSSION

The results of the present investigation show quite clearly that the modified Korringa relation of Eq. (3) adequately relates the observed K_{iso} and T_1 , even when K_{iso} is very temperature-dependent as in Cd. This is the single regular feature of NMR in Cd, and the only irregularity in the Korringa relation is the change of $K(\alpha)$ at the melting point. Recall, as pointed out earlier, any variation of the observed $K(\alpha)$ can have its origin either in a variation of the relative K'/K_s , or in the true exchange enhancement. Therefore, the constancy of the observed $K(\alpha)$ in both the solid and liquid phases of Cd^{113} indicates that K'/K_s is temperature-independent in each phase or the true exchange enhancement is temperature-independent in each phase. Warren, Clark, and Pincus²⁸ have suggested that the true $K(\alpha)$

²⁷ While the change at the melting point is known accurately from the experiment of Ref. 21, the absolute value of the shift in the solid was measured less accurately, and in Sn does not agree with the small extrapolation of the other solid results. Their data are adjusted as shown in Fig. 2.

²⁸ W. W. Warren, Jr., W. G. Clark, and P. Pincus, Solid State Commun. 6, 371 (1968).

may show a temperature dependence arising from a "motional narrowing" of the electronic correlation. However, the evidence for their hypothesis is not strong and this possibility will be disregarded since the change in the observed $K(\alpha)$ in Cd is opposite to their prediction. Therefore, it will be assumed that the true electron exchange enhancement $K(\alpha)$ is independent of temperature, and that the change in the observed $K(\alpha)$ at the melting point can be traced to a change in K'/K_s . All that remains is to discover the size of that ratio, and here the results for Sn^{119} will serve as a guide.

The observed $K(\alpha)$ in Sn^{119} is nearly the same in the solid and liquid states, and its value is in very good accord with predictions^{12,13} of 0.74–0.78. Furthermore, both prediction and observation are in close accord with the generalization¹⁶ that $K(\alpha)=0.75$ is appropriate for liquid metals based on the analysis of NMR in Na^{23} , $\text{Ga}^{69,71}$, In^{115} , $\text{Sb}^{121,123}$, and Bi^{209} . (Proper account was taken of a quadrupolar contribution to the relaxation rate in those liquid metals.) In addition, among the above liquid metals it was concluded¹⁶ that $K'/K_s \neq 0$ only for In^{115} and Bi^{209} , for which values of -10 and -25% , respectively, are appropriate. Consequently, it appears that the observed $K(\alpha)$ in solid and liquid Sn^{119} very nearly reflects the true exchange enhancement and that $K'/K_s \approx 0$ in both the solid and liquid states.

Taking this conclusion as a guide, it is postulated that the observed $K(\alpha)=0.70$ in liquid Cd^{113} represents the true exchange enhancement and that $K'/K_s \approx 0$ in the liquid. However, the change in the observed $K(\alpha)$ at the melting point implies that $K'/K_s \neq 0$ in the solid, and a value of $K'/K_s = -9\%$ is needed to account for the difference between observed $K(\alpha)=0.85$ and the postulated true $K(\alpha)=0.70$.

Because the conclusions above are based upon circumstantial evidence, and it was found that In^{115} has $K'/K_s \approx -10\%$ in the liquid, an alternative hypothesis will be considered. If it is presumed that both Sn^{119} and Cd^{113} have $K'/K_s \approx -10\%$ in the liquid state, then the observed $K(\alpha)$ no longer represents the true $K(\alpha)$ arising from exchange phenomena alone. In fact, values of the true $K(\alpha)$ of 0.65 for Sn^{119} and 0.58 for Cd^{113} are then required to reconcile the assumed $K'/K_s \approx -10\%$ with the observed values of $K(\alpha)$. Continuing the assumption that the true $K(\alpha)$ is the same in both the solid and liquid states implies that K'/K_s is -7% for solid Sn^{119} and -17% for solid Cd^{113} . These implied values of the true $K(\alpha)$ are significantly lower than the generalized value of 0.75, and on this ground this alternative hypothesis is thought unlikely, although not impossible.

VI. CONCLUSIONS

Although the NMR in Cd shows unusual behavior in temperature dependence of K_{iso} and K_{an} , it has been seen that the modified Korringa relation remains a valid link between K_{iso} and T_1 , and this fact has been used to draw inferences of the size of K' which consists of the

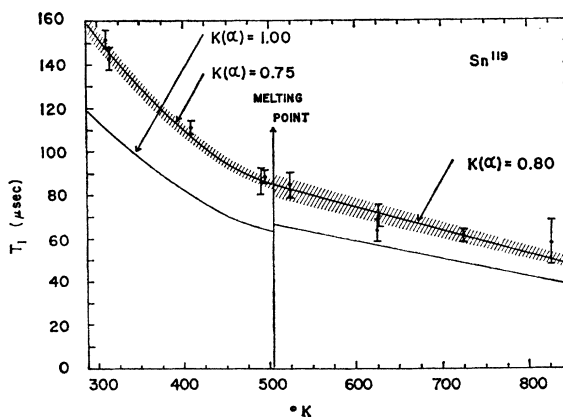


FIG. 5. T_1 versus temperature in Sn^{119} from this work. Same format as Fig. 3. The wider shading in the liquid results from the adjustment made of the K_{iso} data of Knight, Berger, and Heine shown in Fig. 2.

sum of the orbital and core-polarization contributions to K_{iso} . That contribution is found to be small.

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APPENDIX

The relaxation-time measurements reported in this work were performed on a phase-coherent pulsed NMR apparatus which largely follows the design of Clark.²⁹ The high-temperature NMR probe used in these experiments is a simple version of a design by Warren and Clark.³⁰ It features crossed receiver and transmitter coils suitable for use with Clark's pulsed NMR transmitter. The probe was capable of generating an H_1 field in the rotating frame of about 18 Oe, which was sufficient for this experiment. All measurements were made with a conventional two-pulse sequence, and the data were fit by a least-squares computer program to the equation

$$M_z = M_0[1 - A e^{-t/T_1}],$$

where A is determined by the pulse sequence [e.g., $A = 2.0$, for a $(\pi, \frac{1}{2}\pi)$ pulse sequence]. The measurements are difficult for Cd^{113} and Sn^{119} because of the small signal to noise ratio. Without signal averaging, the signal of Cd^{113} is entirely obscured by noise at room temperature and above; the average output signal to noise of the boxcar integrator is only about 10:1 for Cd^{113} at room temperature, 15:1 for Sn^{119} .

²⁹ W. G. Clark, Rev. Sci. Instr. **35**, 316 (1964).

³⁰ W. W. Warren and W. G. Clark, J. Sci. Instr. Series 2, **1**, 1019 (1968).

Samples

The materials for all the samples except tin No. 3 were purchased from United Mineral and Chemical Corporation in powder form with particle size less than 325 mesh (43- μ mesh). Although 43 μ exceeds the skin depth at 77°K, this introduces no distortion of the value of T_1 when the measurements are performed with a phase-coherent pulsed spectrometer, as has been shown theoretically²⁶ and has been verified experimentally.^{26,31} The stated purities were 99.9999%; all materials were of natural isotopic abundance. All samples were sealed in 10-mm i.d., 12-mm o.d. Pyrex tubes. The details of making each sample are different and are given below.

Cadmium. The powder was mixed with an equal volume of silica powder, also less than 325 mesh, placed in the Pyrex tube, evacuated, and sealed with an argon atmosphere enclosed.

Tin No. 1. The tin sample was made by oxidizing the powder in an open test tube in an oven at 200°C for about 8 h. In this way the powder became covered with a durable oxide layer. The powder was then poured into a sample tube, evacuated, and sealed with an argon atmosphere enclosed. The sample was heated to $\approx 360^\circ\text{C}$ ($\approx 128^\circ\text{C}$ above the melting point of tin); the powder still flowed freely.

Tin No. 2. From the same supply of powder as tin No. 1, the powder was mixed with 325-mesh quartz powder in a 50-50% mixture and placed in an unevacuated tube.

Tin No. 3. This sample was made from 200-mesh powder of 99.9% purity obtained from A. D. MacKay Co., New York. Otherwise this sample is identical to tin No. 2.

³¹ D. F. Holcomb, J. A. Kaeck, and J. H. Strange, Phys. Rev. **150**, 306 (1966).

Time-Differential Perturbed Angular-Correlation Experiment for ^{57}Fe in a Ni Host, and a Comparison with the Mössbauer Effect*

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The 122–14-keV γ - γ cascade in ^{57}Fe has been used to detect the precession of the 14-keV state in the hyperfine field produced by a Ni lattice at ^{57}Fe impurity sites. The time-differential perturbed angular-correlation technique was used. The data yield a hyperfine field of -267.5 ± 2.7 kG at room temperature. The magnitude is in agreement with Mössbauer measurements; the sign is determined here for the first time. The data also yield a half-life of 99.3 ± 0.5 nsec for the 14-keV state, and an anisotropy coefficient $A_2 = -0.0187 \pm 0.0015$ for the 122–14-keV cascade. In addition, the data show the absence of time-dependent perturbations over the experimental time interval of 400 nsec. Based on this, application to the study of critical field fluctuations is discussed.

1. INTRODUCTION

TIME-DIFFERENTIAL perturbed angular correlation (TDPAC) was originally used to measure magnetic moments of relatively long-lived (10–1000 nsec) excited states of nuclei by use of known applied fields. The technique consists essentially of a delayed coincidence measurement on a nuclear γ -ray cascade, in which the Larmor precession of the intermediate-state nucleus in the applied field is directly observed as oscillations on the lifetime curve. An excellent early example of such measurements is the work of Matthias *et al.*¹ on ^{111}Cd and ^{181}Ta . It can be seen from this, as well as more recent cases,^{2,3} that among perturbed

angular-correlation methods, TDPAC is at once the most precise and the most clearly interpretable. A possible exception is resonance destruction of angular correlations.⁴

In the last few years, TDPAC has been applied to internal fields at impurity nuclei in ferromagnetic hosts. In this role, TDPAC yields field values if the excited-state moment has been independently measured. Unlike nuclear magnetic resonance, and like Mössbauer and nuclear polarization experiments, TDPAC is very sensitive (impurity concentrations of 10^{-5} or better are typical) and does not suffer from rf absorption difficulties. TDPAC is potentially superior to Mössbauer experiments for low fields because a number of cascades have sensitivities of ~ 100 G,⁵ while the best Mössbauer

* Work supported in part by the U. S. Atomic Energy Commission.

† Brandeis University Undergraduate Research Participant.

¹ E. Matthias, L. Boström, A. Maciel, M. Salomon, and T. Lindqvist, Nucl. Phys. **40**, 656 (1962).

² *Perturbed Angular Correlations*, edited by E. Karlsson, E. Matthias, and K. Siegbahn (North-Holland Publishing Co., Amsterdam, 1964).

³ *Hyperfine Structure and Nuclear Radiations*, edited by E. Matthias and D. A. Shirley (North-Holland Publishing Co., Amsterdam, 1968).

⁴ E. Matthias, D. A. Shirley, N. Edelstein, H. J. Körner, and B. A. Olsen, Ref. 3, p. 878.

⁵ J. Alonso and L. Grodzins, Ref. 3, p. 549.