PHYSICAL REVIEW B VOLUME 35, NUMBER 10 1 APRIL 1987

Knight shift of ^{111}Cd impurities in liquid selenium

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(Received 13 August 1986)

The Knight shift of dilute ^{111}Cd dopants in liquid selenium has been measured at $\sim 800\,^{\circ}\mathrm{C}$ by the gamma-gamma perturbed angular-correlation method. The Knight shift is found to be zero with an uncertainty of 0.5%. This result indicates that magnetic hyperfine exchange with paramagnetic dangling bonds is not the dominant mechanism for nuclear relaxation of ^{111}Cd. Instead, ^{111}Cd relaxation in chalcogenide liquids must be attributed to the interaction of the nuclear quadrupole moment with fluctuating electric field gradients.

INTRODUCTION

The nuclear relaxation of very dilute ^{111} Cd impurities in liquid $\mathrm{Se}_x\mathrm{Te}_{1-x}$ alloys has been investigated by Gaskill *et al.*[1] using gamma-gamma perturbed angular correlation (PAC) spectroscopy. The decay rate λ of the ^{111}Cd angular correlation is found to depend on the concentration of paramagnetic dangling bonds in the liquid, but it has little explicit temperature or concentration dependence. The decay rate is much faster than PAC decay rates observed[2,3] for Xe in liquid Te or typical NMR nuclear relaxation or PAC decay rates in liquid[4-7] and nonmagnetic solid[4,5,8] metals. One hypothesis suggested by these and other observations is that the Cd atom is bound in close proximity to a free electronic spin and that the dominant contribution to λ is the magnetic interaction between the Cd nuclear spin and the electronic spin. The possibility that a Cd atom dissolved in liquid chalcogens is always associated with a paramagnetic center has a number of important implications about the chemistry of dopants in liquid and amorphous chalcogenide semiconductors. The object of the experimental study described here was to test that magnetic interaction hypothesis, and it is found to be incorrect. The ^{111}Cd decay is apparently due not to magnetic fluctuations but to electric-field-gradient fluctuations that are closely associated with bond defects in the system.

THEORETICAL PRINCIPLES

Nuclear magnetic resonance is normally the technique of choice for measuring Knight shifts.[4] However, the proposed magnetic relaxation mechanism would cause an extremely rapid T_1 for the (ground state) ^{111}Cd NMR isotope, making its resonance unresolvable. Consequently, PAC was used for this measurement. PAC has been used in some instances for Knight shift determination[5] and is sufficiently accurate to detect shifts as large as 2%.

In this experiment, two gamma rays emitted following decay of ^{111}In to ^{111}Cd are detected. The emission probability of the second gamma ray after time t and at angle θ with respect to the direction of the first gamma ray is given by[9]

$$W(\theta,t)d\Omega=\frac{e^{-t/\tau_N}}{\tau_N}\left[1+\sum_{k=2,4}A_kC_k(\theta,t)\frac{d\Omega}{4\pi}\right], \qquad (1)$$

where τ_N is the lifetime of the intermediate state,[10] A_k is a nuclear anisotropy parameter,[10] and $C_k(\theta,t)$ is a function that is unity when θ and t are both zero and ≤ 1 otherwise. A_4 is very small, and the $k=4$ term is neglected. In the motional narrowing approximation[11] and in absence of external fields,

$$C_2(\theta,t)=P_2(\cos\theta)\exp(-\lambda t), \qquad (2)$$

where $P_2(\cos\theta)$ is a Legendre polynomial, and the decay rate λ depends on the correlation time and average squared frequency of the hyperfine interaction between the ^{111}Cd nucleus (in its intermediate state) and its environment in the liquid. In general both magnetic and quadrupolar interactions contribute to λ. With an external magnetic field B_0 perpendicular to the detector plane,[9]

$$C_2(\theta,t)=P_2[\cos(\theta-2\pi\nu t)]\exp(-\lambda t), \qquad (3)$$

where $\nu=\mu B/2\pi I$ is the Larmor frequency in the effective magnetic field,

$$B=B_0(1+K-\alpha). \qquad (4)$$

α is a small diamagnetic shielding parameter estimated[12] to be approximately 0.05%, and the Knight shift K is due to interaction with electron spins.

If magnetic hyperfine exchange between the electronic spin S and the nuclear spin I is the dominant contribution to nuclear decay, then[11]

$$\lambda=\tfrac{3}{2}\langle\omega_S^2\rangle\tau_S. \qquad (5)$$

τ_S is the correlation time of S at the nucleus, and $\langle\omega_S^2\rangle^{1/2}$ is the rms interaction frequency. τ_S is known for dangling bonds in liquid Se.[13] It is found[1] that for ^{111}Cd in liquid Se, λ/τ_S is independent of temperature, with an implied value of $9.5\times10^{8}\ \mathrm{sec}^{-1}$ for $\langle\omega_S^2\rangle^{1/2}$. This is typical of exchange frequencies for first-neighbor hyperfine exchange. For this interaction

$$K=\frac{h\langle\omega_S\rangle\mu_B}{2k_BT}\left|\frac{I}{\mu}\right| . \qquad (6)$$

If the exchange is isotropic, $\langle\omega_S\rangle\simeq\langle\omega_S^2\rangle^{1/2}$. At 1000 K, $|K|$ should be approximately 2.2% for ^{111}Cd in liquid Se and should vary as T^{-1}.

EXPERIMENTAL PROCEDURE AND RESULTS

Four NaI scintillation detectors were mounted in the vertical center plane of a 6-in. electromagnet. The pole caps were tapered to 2 in. in diameter with a 1-in. gap at the center, giving a central field of 16 kG. The NaI crystals were 6 cm from the center of the magnet and were attached to the photomultiplier tubes with 25-cm-long plastic light pipes. Because of the geometry of the magnet yoke, the detectors were arranged at angular intervals of 135°, 45°, 135°, and 45°, respectively. Apart from the detector geometry, the PAC apparatus is a conventional four-detector spectrometer described elsewhere.[1,14] Each detector could detect both first and second gamma events, and a total of eight independent coincidence spectra could be accumulated simultaneously. After subtracting an approximately time-independent random count background, the coincidence spectrum from detectors at relative angle θ_{ij} is proportional to $W(\theta_{ij},t)$ with an "effective" anisotropy $\overline{A}_2$ that depends on sample and/or detector geometry.

The ^{111}In tracer was obtained from New England Nuclear/Dupont Corporation as a carrier-free solution in dilute HCl. In order to determine K, room-temperature PAC spectra were first measured for the solution, which is diamagnetic and for which K is zero. For ^{111}In*Se* samples, a selenium pellet was placed in a fused silica vial to which a few drops of the ^{111}In solution were added. The vial was heated until all water had evaporated, and it was then evacuated and sealed. The samples are typically 3–5 mm high when molten. During measurement, these samples were heated by a small nichrome-wound water-cooled heater mounted in the magnet gap. An appropriately made sample could be used for 7–10 days before it would become too weak.

Normally, it is most convenient to compare experiment with theory by forming a ratio of appropriate coincidence spectra so that the exponential lifetime decay and experimental parameters such as detector efficiencies, counting time, etc., cancel.[1,15] These cancellations occur only if the sample can be mounted along the detector plane central axis. Unfortunately, it was impossible to mount a furnace within the small magnet gap so that the sample could be positioned perpendicular to the detector plane. Instead, the furnace was mounted so that the sample tube was vertical and, consequently, lay parallel to the detector plane. Unavoidable differences between samples, variable positioning, angular-dependent absorption of gamma rays by the apparatus, etc., caused slight but non-negligible deviations from ideal cylindrically symmetric geometry. In order to minimize all such errors, each coincidence spectrum was fitted individually. τ_N and λ were fixed at their experimentally determined values; ν and $\overline{A}_2$ were taken as fitting parameters. We also found it necessary to allow for "baseline drift" caused by instrumental effects and, at high count rates, by the time-dependent random count rate.

Typical spectra and computer fits for ^{111}Cd in aqueous solution at room temperature and in liquid Se at ≈800 °C are shown in Fig. 1. Since the same experimental procedure and analysis was used for the aqueous and selenium samples, it is expected that any systematic errors should be the same for each.

The magnetic field was measured as a function of vertical distance z from the spectrometer (i.e., magnet and detector plane) center using a high-precision Hall probe. Over the central 1 cm, the field was homogeneous within the precision (better than 0.1%) of the probe. The total $B(z)$ calibration error is 0.2% and 1 mm in positioning of the Hall sensor. Time calibration of the spectrometer was accurate to approximately 0.1%. Typically, PAC measurements were made and the Larmor frequency determined at several z positions. The sample vials remained always at the center of the furnace, and the furnace was moved up or down within the magnet gap. It is convenient to define a quantity $g(z)$ that is equal to the Larmor frequency at z divided by the central magnetic field. The effective gyromagnetic ratio $\gamma=\nu/B_0$ is equal to $g(0)$. $g(z)$ for aqueous samples is shown in Fig. 2. Each

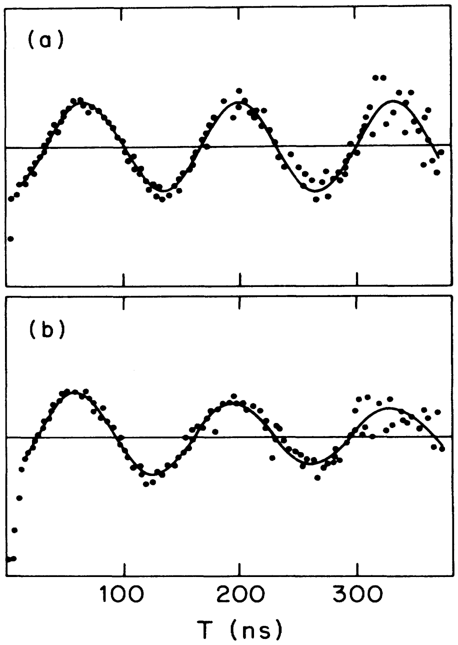

FIG. 1. Typical PAC spectra for ^{111}Cd in (a) aqueous (dilute HCl) solution and (b) in liquid selenium at 800 °C. These spectra are derived from the raw coincidence spectra by subtracting a constant random count background, and multiplying by $\exp(t/\tau_N)$. The detectors are at 180° angular separation. The channel width is 2.98 ns and the external magnetic field is 15.9 kG. Solid lines are computer fits discussed in the text. $\overline{A}_z$ is -0.10 for each fit.

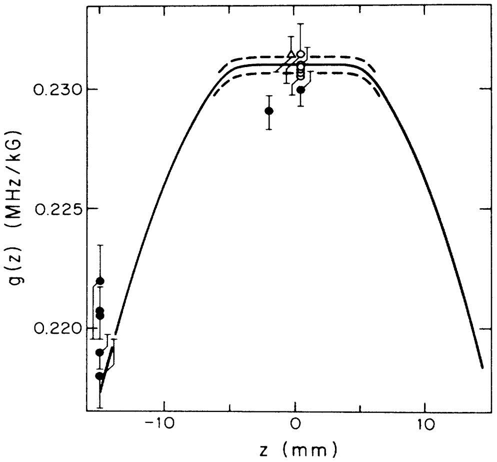

FIG. 2. Ratio of ^{111}Cd Larmor frequency to central magnetic field vs vertical distance of liquid center from spectrometer center—for Cd in diamagnetic aqueous solution at room temperature. The two samples shown by open symbols were approximately 3 mm high. The sample shown by filled symbols was 11 mm high. The solid line is proportional to the magnetic field $B(z)$ with $g(0)=0.2310$ MHz/kG. Dashed lines show limits of statistical uncertainty for $g(0)$.

point represents an average of $g(z)$ for the eight spectra accumulated in a (typically 24-h) measurement. Error bars show the statistical standard deviation of that average. Data represented by open symbols were from samples in which the liquid was approximately 3 mm high and positioned so the center of the liquid was within 1 mm of the spectrometer center. The filled circles are data from an 11-mm-long sample. Since a significant fraction of this sample was always outside the homogeneous field region, the data are not quantitatively meaningful, but they do illustrate that $g(z)$ has semiquantitatively the same z dependence as the magnetic field. From the data shown by open symbols, γ is found to be 0.2310(4) Mhz/kG, in good agreement with the currently accepted value of 0.232(1) Mhz/Kg.[16] The error is statistical uncertainty only.

$g(z)$ for liquid ^{111}In*Se* samples is shown in Fig. 3. Positioning was much more difficult for these samples, because the liquid may not have been at the bottom of the sample vial during measurement. A commonly encountered experimental problem[17] is that liquids heated in small vials occasionally rise to the top. This phenomenon is probably caused by temperature-dependent surface tension but is not well understood. Unfortunately, there is no simple way to tell where the liquid sits in a vial during a measurement. The sample vials could not be made arbitrarily short in order to reduce the uncertainty in position. Very short vials could not be sealed without heating the sample significantly. Such heating apparently promoted a chemical reaction that prevented the indium from dissolving completely in molten selenium. PAC spectra from these samples clearly included a static component as well as the expected liquid spectrum. Such data were discarded.

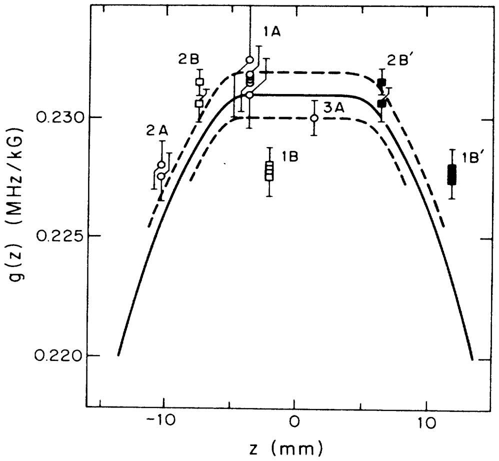

FIG. 3. Ratio of ^{111}Cd Larmor frequency to central magnetic field vs vertical distance of liquid center from spectrometer center—for dilute Cd in liquid selenium at 760 °C±20 °C (A), 800 °C±10 °C (B). Sample A (circles) is sealed in a 25-mm-long fused silica vial. Sample B (squares) is sealed in a 17-mm-long vial. The solid line is proportional to the magnetic field $B(z)$ with $g(0)=0.2310$ MHz/kG. Dashed lines show limits of experimental uncertainty. Data sets from sample A (B) are labeled as $1A$, $2A$, and $3A$, ($1B$,$2B$) in the order in which they were measured. The liquid is assumed to be at the bottom (top) of its vial for open (closed) symbols, respectively.

Liquid selenium samples A and B, for which data are shown in Fig. 3, were contained in 25- and 17-mm-long vials, respectively. The furnace power was current-controlled, and the temperature varied somewhat during measurement. Sample A temperatures were 760 °C ±20 °C. Sample B was 800 °C±10 °C. Temperature variations of this magnitude should not affect the PAC spectra. The z position of the open symbol in Fig. 3 is computed under the assumption that the liquid was at the bottom of the vial during measurement. For sample A, it is clear from the z dependence that this assumption must be correct. The last data point, $3A$, falls slightly low with respect to the first two sets, and it is possible that the liquid moved upward into a region of smaller magnetic field during this measurement. $3A$ is only two standard deviations low, however, and this could be only a statistical fluctuation. The first set, $1B$, of data for sample B do not agree well with other measurements. Both $1B$ and $2B$ would be in reasonable agreement with other data if liquid B were near the top of its vial during measurement. The solid squares in Fig. 3 show the B data under that assumption. The location of the vial during accumulation of data set $2B$ was carefully chosen so the liquid would be in or very near the central maximum field independent of its location within the vial. For $2B$, g agrees well with the central-field data of sample A.

Using data sets $1A$, $3A$, and $2B$, γ is found to be 0.2310(10) MHz/kG. In view of the possibility that $3A$ and $2B$ may not be well centered, the uncertainty is taken as the maximum statistical error that would result if $3A$ and/or $2B$ were excluded.

SUMMARY AND CONCLUSIONS

PAC was used to measure the effective gyromagnetic ratio γ of dilute ^{111}Cd (resulting from decay of ^{111}In) dissolved in liquid Se at ~800 °C and in aqueous solution at room temperature. The difference gives the Knight shift of ^{111}Cd in liquid Se. The shift is found to be zero with an uncertainty of 0.5%. This result casts serious doubt on the hypothesis[1] that ^{111}Cd nuclear relaxation is caused by magnetic hyperfine exchange with a nearby electronic spin. That exchange interaction is expected to produce a Knight shift of approximately 2% at 800 °C. The magnetic exchange model has also been brought into question by Lin *et al.*,[18] who found that the electronic spin relaxation time τ_S in liquid $Se_{0.5}Te_{0.5}$ is an order of magnitude smaller at a given spin density than τ_s in liquid selenium. That finding contradicts a key assumption of the magnetic exchange model—that τ_s depends only on spin density.

The implication of this investigation is that the relaxation of ^{111}Cd in liquid chalcogenide semiconductors is not due to magnetic interaction but is instead caused by fluctuating electric field gradients (EFG) interacting with the nuclear quadrupole moment. This is an important result. It removes a significant interpretational ambiguity and provides some confidence that the EFG-correlation times[1] computed for these liquids are meaningful. The similar temperature dependence of the spin and Cd-quadrupolar correlation times in liquid Se and for the Cd- and Cu-quadrupolar correlation times[18] in liquid $Se_{0.5}Te_{0.5}$ suggest that all these times are related. The relationship of the various correlation times to spin density leads to the further speculation that both spin and EFG relaxation are controlled in some fashion by defects, with the majority of the defects being magnetic dangling bonds at high temperatures and nonmagnetic ones at low temperature. Such nonmagnetic defects as negatively charged dangling bonds and positively charged chain branches are commonly believed to exist in chalcogenide glasses,[19,20] but experimental information is presently indirect and ambiguous. Better understanding of these relaxation processes could lead to more direct experimental methods for investigating nonmagnetic defects.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation under Grant No. DMR-8320547.

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