Lattice location of ^{12}B in aluminum and copper at 77 K†

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Polarized ^{12}B was produced in the reaction ^{11}B$(d, p)^{12}$B and recoiled into single-crystal samples of aluminum and copper. Resonance depolarization of the ^{12}B for the aluminum (copper) crystal oriented with each of its principal crystallographic directions in turn parallel to an externally applied holding field showed that 90–100% (76–100%) of the boron occupies the octahedral interstitial site.

INTRODUCTION

The resonance depolarization of ^{12}B ($I^{\pi} = 1^+$, $t_{1/2} = 20.4$ msec) implanted in a considerable number of metallic and semiconductor hosts at room temperature has been observed.[1] In fcc metals, a single resonance line is observed. This is indicative of a high-symmetry crystallographic site with little or no quadrupole splitting of the magnetic substates. Therefore, there are three possible sites which the ^{12}B can occupy: substitutional, octahedral (at the center of the cubic lattice), and tetrahedral interstitial (one-fourth of the distance along a body diagonal).

The particular site occupied by ^{12}B can be distinguished using a single-crystal host. The magnitude of the nuclear dipole-dipole interaction is proportional to $(3\cos^2\theta - 1)$, where θ is the angle between the direction of the applied magnetic field H_0 and the position vector of each of the host nuclei with a nonzero magnetic moment.[2] The magnitude of the interaction can be calculated using the method of moments.[2] Each of the above mentioned high-symmetry sites would produce a different second moment (M_2) value and give rise to a different linewidth for each of the major crystallographic directions oriented in turn parallel to H_0.

We chose initially to determine the site of ^{12}B implanted in aluminum and in copper because a high degree of polarization of the ^{12}B is retained in these systems.[1] The full width at half-maximum (FWHM) linewidths (assuming a Gaussian for the line shape) for each of the high-symmetry sites in the ⟨100⟩, ⟨110⟩, and ⟨111⟩ are given by $2.36 \times (M_2)^{1/2}$,[3] where M_2 is calculated using the expression given in Ref. 2.

Only spin-spin interactions between ^{12}B and host (^{27}Al or ^{63}Cu and ^{65}Cu) nuclei are considered. The computation of M_2 for the substitutional site was carried out for 30 nearest neighbors (nn); octahedral site, 36 nn; tetrahedral site, 22 nn. A rough estimate was also made of the small contribution to M_2 from the nuclei in the remainder of the crystal. A tabulation of the calculated linewidths is given in Table I.

EXPERIMENTAL DESCRIPTION

Polarized ^{12}B was produced in the reaction ^{11}B$(d, p)^{12}$B at a deuteron energy of 1.5 MeV and beam current of 3–5 μA using the Lockheed 3-MeV Van de Graaff. The experimental setup is shown in Fig. 1. The plug holding the crystal can be replaced either by a small heater for experiments in the temperature range $300 \lesssim T \lesssim 770$ K or by a glass cryostat for experiments in the temperature range $77 \lesssim T \lesssim 300$ K. The target of unenriched boron is evaporated to a thickness ≈60 μg cm^{-2} on a copper backing. It must be stressed that the ^{12}B is polarized in the nuclear reaction itself. The polarization P is defined in terms of the $2I+1$ nonthermal equilibrium substate populations p_m as

$$P = \sum_m m p_m$$

$$= p_1 - p_{-1} \text{ for } I = 1,$$

where the p_m are normalized by $\sum_m p_m = 1$.

In the nuclear reaction the ^{12}B receives a maximum kinetic energy ≈450 keV allowing it to recoil out of the ^{11}B target. However, since the ^{12}B originates from different depths of the target, is populated through different excited states and has a rapid angular dependence of energy, the ^{12}B recoils are heteroenergetic. Prior experiments have shown that ^{12}B nuclei recoiling at an angle of 45° to the deuteron beam direction are the most highly polarized.[4] Thus the ^{12}B beam was collimated to within ±5° at this recoil angle and implanted in a single-crystal stopper.

The aluminum and copper was supplied by Materials Research Corp. in the form of 2.5-cm-diam cylinders with purities of 99.999%. Slices 2 mm thick were cut with a string saw and chemically etched to a final thickness ≈0.75 mm in order to remove surface damage arising from the cutting process. The crystals were oriented such that ^{12}B could be implanted while each of the major

TABLE I. Resonance linewidths for aluminum and copper.

Crystal	Crystal direction	Linewidth, FWHM (kHz) Substitutional	Tetrahedral interstitial	Octahedral interstitial	Experiment (Γ) $T=77$ K
Al	⟨111⟩	3.54	9.98	1.94	2.87± 0.15
Cu		3.33	9.37	1.82	3.00± 0.20
Al	⟨110⟩	3.59	8.83	5.12	4.28± 0.35
Cu		3.37	8.28	4.81	4.64± 0.31
Al	⟨100⟩	2.62	2.50	9.58	8.10± 0.32
Cu		2.45	2.35	8.99	7.25± 0.25

crystallographic directions was in turn positioned parallel to the 5-kOe uniform holding field. This field was produced by a 30.5-cm Varian magnet and stabilized with the aid of a proton resonance fluxmeter inserted near the center of the 7.6-cm magnet gap. An rf depolarizing field H_1 perpendicular to H_0 was supplied by a coil surrounding the individual crystal host coupled to a 100-W radio transmitter and voltage-tuned oscillator. The ratio of the proton resonance frequency and the rf depolarizing frequency were kept constant by a computer-controlled servo loop. The instrumental linewidth of the resonance spectrometer is less than 50 Hz.

The ^{12}B decays by β emission which is anisotropically distributed for $P \neq 0$. In the nuclear reaction the polarization is created parallel to H_0; therefore, with two counter telescopes placed near the magnet pole faces (as shown in Fig. 1) and on either side of the aluminum crystal, it was possible to measure the change in polarization directly. Each of the counter telescopes consists of two 2-cm-diam scintillation detectors operating in coincidence in order to overcome the large background from bremsstrahlung emitted by β rays stopping in the vicinity of the crystal hosts. In this way the signal-to-background ratio is increased from about 1:1 to 20:1. For the direction parallel to the polarization the count rate is proportional to $1-P$. Thus the ratio of the count rates in the two telescopes or β asymmetry is proportional to $(1+P)/(1-P)$. Clearly, we are observing the longitudinal component of the polarization here. An effective doubling of the β asymmetry can be obtained using the adiabatic fast passage (AFP) technique.[5] This allows the rapid reversal of the ^{12}B spins through 180°, which leads to a reverse β asymmetry proportional to $(1-P)/(1+P)$. Thus, the ratio of β asymmetry before and after AFP is $(1+P)^2/(1-P)^2$. This expression is referred to as the change in anisotropy (A).

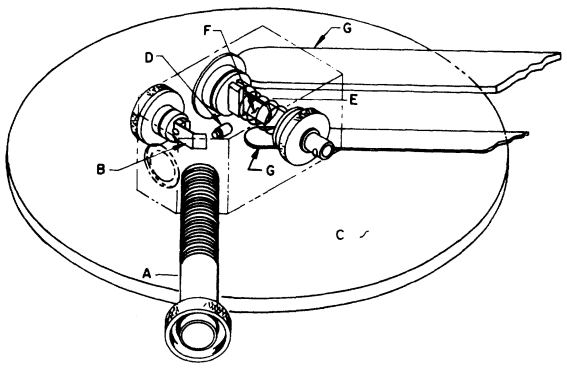

FIG. 1. Scattering chamber: deuterons enter through tube (A); target (B); magnet pole face (C); ^{12}B beam collimator (D); rf depolarizing coil (E); host crystal (F); coincidence counter telescopes (G).

Since neutrons and high-energy γ rays produced in the ^{11}B$(d,p)^{12}$B reaction contribute a high background counting rate with the beam on, even with the counter telescope detection system, an irradiate/count sequence is employed. The sequence of deuteron bombardment, counting, spin reversal, and depolarization can be best explained with the aid of a timing chart, shown in Fig. 2. The deuteron beam is turned on for 40 msec and then turned off while counting of the delayed β-ray activity from the host proceeds. While irradiation is in progress and during the count period, a depolarizing radiofrequency field is applied to the host. Counts from the detectors are stored in the memory locations of an SEL 810A computer according to the frequency of the depolarizing field. The β asymmetry is continuously computed and displayed as a function of the frequency of the depolarizing field. Before alternate count cycles, the ^{12}B spins are reversed by the adiabatic fast passage technique. The rapid sweep in frequency as well as the change in amplitude of the radiofrequency field is controlled by the computer. Counts from the normal and reversed spin directions are stored separately, and normal and re-

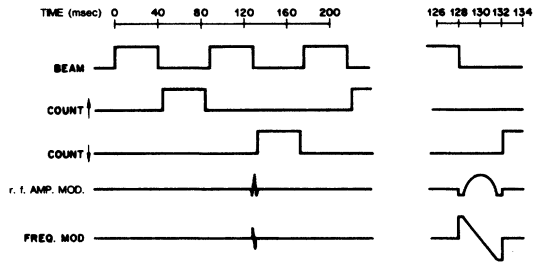

FIG. 2. Timing chart showing sequence of deuteron bombardment, counting, spin reversal (AFP), and depolarization.

verse asymmetries as well as saturation of the resonance are computed.

RESULTS

Figures 3 and 4 show plots of the FWHM linewidth of the resonance at $T=77$ K in each of the $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ versus H_1 for aluminum and copper, respectively. The spectra obtained at the lowest depolarizing fields took approximately 24 h run time to accumulate at 4000 sec^{-1} in each telescope and represent (5–10)% saturation of the resonance. On the other hand, data obtained for $H_1 \approx 200$ mG represent ≈75% saturation and required 2–3 h of run time.

Typically a spectrum is accumulated during the implantation of $\approx 10^{10}$ cm^{-2} ^{12}B nuclei (which decay to ^{12}C). The highest-energy implants have a projected range in Al and Cu ≈1 μm. Assuming that the boron is distributed evenly throughout a 1-μm-thick layer, the ^{12}C impurity concentration in the layer after several runs is approximately 10^{-9} to 10^{-8}. There are only a few thousand ^{12}B atoms in the implanted layer at any one time. Clearly, spin-spin interactions between ^{12}B nuclei (^{12}C has no spin) can be neglected in the calculation of M_2. Also under these circumstances, very little radiation damage is likely to accrue to the crystals. The linewidths within experimental error increase linearly with H_1. Thus, a straight-line least-squares fit to each set of data produces an intercept Γ (given in the last column of Table I) when extrapolated to $H_1=0$, which is to be compared with the calculated values in Table I.

For both aluminum and copper the Γ values are

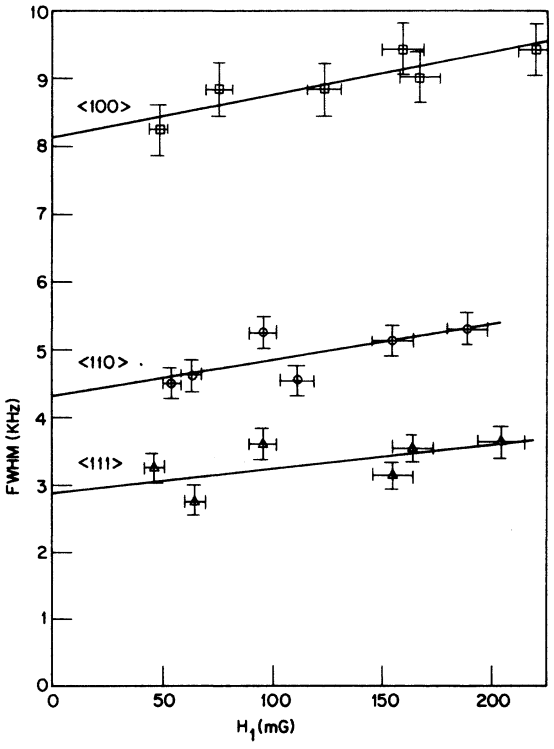

FIG. 3. Linewidth vs depolarizing rf field amplitude for aluminum at $T=77$ K with each of the $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ oriented in turn parallel to the holding field H_0, which was 5 KG, giving a ^{12}B resonance frequency of ≈3.8 MHz.

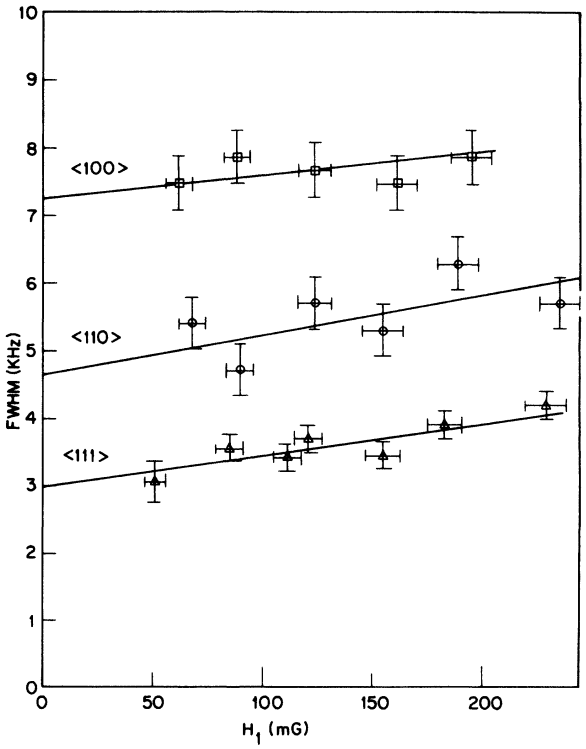

FIG. 4. Linewidth vs depolarizing rf field amplitude for copper at $T=77$ K with each of the $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ oriented in turn parallel to the holding field H_0.

in substantial quantitative agreement only with the octahedral-site calculations. In view of the assumption of a Gaussian line shape this agreement is quite good for two of the three crystal directions. In ⟨111⟩, however, the experimental linewidths are (50–60)% greater than the calculated values.

DISCUSSION

Assuming that the octahedral site is indeed occupied by the ^{12}B requires an explanation of the above discrepancies in intercept values in ⟨111⟩ together with other anomalous features exhibited in linewidth-vs-H_1 curves of Figs. 3 and 4. These are a high degree of saturation of the resonance for $H_1 \ll (M_2)^{1/2}$ and rf broadening of the resonance 2–4 times greater than would be expected for an inhomogeneously broadened line.

The above-described phenomena, except for the Γ values in ⟨111⟩, can be accounted for if the ^{12}B gives rise to a homogeneously broadened line by diffusing interstitially with a jump time $\tau \ll t_{1/2}$. As τ decreases Γ will be reduced in value because of the fluctuations in the dipolar field[6] at the ^{12}B nucleus. Diffusion effects give rise also to enhanced rf (or power) broadening and to the saturation of the resonance for $H_1 \ll (M_2)^{1/2}$.[7]

Alternative experiments were carried out to confirm the homogeneous nature of the line shape. The counting sequence was modified so that a constant-frequency depolarizing field in the wings of the resonance was applied during the beam-on period. This resulted in retention of the lineshape for annealed polycrystalline samples of aluminum and copper, but a reduction in its amplitude, again confirming the homogeneous nature of the broadening. Data obtained at $T = 300$ K gave Γ values (10–45)% smaller than those at $T = 77$ K, together with rf broadening of the resonance 5–10 times greater than for an inhomogeneously broadened line. Experiments performed above room temperature show that the resonance narrows to ≈50 Hz in the region of 540 K. This extreme narrowing can be accounted for only by diffusion effects. Results on these and further experiments on ^{12}B implanted in aluminum and copper together with the determination of the activation energy for diffusion of ^{12}B in these metals will be reported in detail at a later date. The most likely cause of broadening in ⟨111⟩ is damage in the lattice produced by the thermalizing process of the incoming ^{12}B. Point defects existing 1 or 2 lattice parameters distant from the ^{12}B would be sufficient to create a small electric field gradient at the ^{12}B site and hence a quadrupole broadening (QB) of the line. For a random QB ~ 2–3 kHz, the linewidth for ⟨111⟩ would be strongly affected, whereas the linewidth for ⟨100⟩ would be affected only marginally.

Thus the data can be most satisfactorily accounted for if the ^{12}B contributing to the resonance line occupies an octahedral interstitial site in both aluminum and copper.

A measurement of the fraction of ^{12}B occupying such sites was made using the AFP technique. This allows the determination of the polarization by measuring the change in anisotropy of the β emission as described previously. In this case the depolarizing field H_1 is reduced to zero. For the polycrystalline metals Pt, Pd, Ag, and Al at $T = 300$ K and the semiconductors Si and Ge above $T = 675$ K, $A = 1.45 \pm 0.03$ (or $P = 0.093 \pm 0.05$). The error is a measure of how experimental parameters can affect the polarization, e.g., target condition, beam position, crystal surface condition. We have not observed any values higher than this. Thus, we take $A = 1.45$ to indicate that all the boron in a given crystal contributes to the resonance line and thus occupies a cubic crystallographic site. Since aluminum is one of the four fcc metals given above, we propose that (90–100)% of the ^{12}B takes up the octahedral interstitial site.

In copper at $T = 77$ K, $A = 1.38 \pm 0.03$ ($P = 0.08 \pm 0.05$), giving an increase of approximately 0.1 in P from the room temperature value. On cooling from room temperature to $T = 77$ K the spin-lattice relaxation time T_1 can be expected to increase by a factor of 4 for a system obeying the Korringa relationship. Thus the value of A at $T = 77$ K must be virtually unaffected by T_1 effects, and the percentage of ^{12}B atoms on cubic sites in copper = 83% ± 7%. This figure may be a lower limit, since it is entirely possible that for a completely oxide-free copper surface (extremely difficult to prepare in practice) A would have its maximum possible value. In this case it is more realistic to state that (76–100)% of ^{12}B occupies cubic sites in copper. If indeed, less than 100% of ^{12}B takes up a cubic site, then the remainder are probably associated with radiation-damaged or random sites where the crystallographic symmetry is sufficiently low to cause rapid ^{12}B depolarization.

ACKNOWLEDGMENT

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[2]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. P., Oxford, 1961), p. 97 ff.

[3]Reference 2, p. 107.

[4]L. Pfeiffer and L. Madansky, Phys. Rev. 163, 999 (1967).

[5]Reference 2, p. 34 ff.

[6]N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948). For a review see D. C. Ailion, in *Advances in Magnetic Resonance*, edited by J. S. Waugh (Academic, New York, 1971), Vol. 7, and references quoted therein.

[7]Reference 2, p. 517 ff.