

Diffusion of Boron in Copper by Direct-Exchange Mechanism

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The behavior of B impurities implanted into Cu single crystals has been investigated by means of β radiation detected nuclear magnetic resonance and cross-relaxation spectroscopy. Diffusion of substitutional B (B_s) in Cu is observed in the temperature range of $T = 600\text{--}750$ K. By combining information from new and formerly published data it is shown that this diffusion is not mediated by any other defect; it rather takes place by a direct site exchange between B_s and neighboring Cu atoms. To our knowledge B_s in Cu is the first system for which this long discussed diffusion mechanism has been established experimentally. [S0031-9007(96)01798-X]

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Three basic microscopic mechanisms are usually considered for the diffusion of substitutional impurity or host atoms in crystals: the vacancy mechanism, where the moving atoms jump into a neighboring vacancy, the interstitialcy mechanism, where a substitutional atom is pushed from its site by an arriving interstitial atom and regains a new substitutional position in similar fashion, and the direct-exchange (DE) mechanism, where two neighboring atoms or a ring of atoms simultaneously interchange their positions [1–5]. While the first two so-called indirect mechanisms are well established for a multitude of systems, the DE process has never been verified experimentally until now. This is in contrast to theoretical calculations which give arguments for this mechanism to occur in semiconductors [6], ionic crystals, and metals [7,8]. In this Letter we report the first experimental identification of vehicle-free substitutional diffusion by the DE mechanism.

The system under study is single-crystalline Cu with isolated B impurities introduced by ion implantation. Our discussion will be partly based on recently measured data, but to a large extent will make use of results by McDonald and McNab [9] and of our group [10] that have been published several years ago but whose relevance for the diffusion process has not been discussed before. The experimental technique in all studies was the so-called β radiation detected nuclear magnetic resonance (β NMR), partly in conjunction with cross-relaxation (CR) measurements. After introducing the method we will present the data and show that at appropriate temperatures part of the implanted B nuclei do occupy substitutional lattice sites and are mobile on these sites. In the remainder of the paper we will discuss the possible contributions of any defect mediated diffusion and will see that these can be excluded, leaving the DE as the only remaining diffusion mechanism. Already at this stage we want to point out, however, that we have no way to decide whether the individual jump process involves just a substitutional boron (B_s) and one neighboring Cu atom, or a ring of atoms containing the B_s and n Cu atoms (general arguments [3]

and molecular dynamics simulations for pure Cu [7] favor the ring exchange with typically five Cu atoms). Even a third scenario, where a ring of Cu atoms moves around a B_s , which itself does not actually change its position but acts as a catalyst for the ring diffusion, would be undistinguishable.

β NMR is a well established nuclear technique in defect physics [11,12]; we therefore restrict ourselves to a brief outline. β active ^{12}B probe nuclei with a lifetime $\tau_\beta = 29.3$ ms and a nuclear spin $I = 1$ were created in the nuclear reaction $^{11}\text{B}(d, p)^{12}\text{B}$ in a thin boron-target foil irradiated with a beam of 1.5-MeV deuterons from an ion accelerator. The recoil ejected ^{12}B nuclei were spin polarized along an external magnetic field \mathbf{B}_0 by selection of a recoil angle of $45 \pm 8^\circ$ relative to the incident beam and implanted into the Cu crystal with broadly distributed energies from 0 to 450 keV. Thus the concentration profile was rather homogeneous up to a maximum depth of about $0.7 \mu\text{m}$. The total number of ^{12}B nuclei being simultaneously present in the sample never exceeded 10^4 , corresponding to a concentration of 10^8 cm^{-3} or a mean separation by about 10^5 lattice constants. Not only the probe nuclei themselves but also their respective implantation-damage cascades were thus well isolated from each other. The detected quantity was the angular β -decay asymmetry which is proportional to the nuclear spin polarization P .

Two different experimental approaches have been applied. McDonald and McNab [9] observed resonance signals caused by irradiation of a depolarizing radio frequency field. These data we will henceforth refer to as NMR spectra. In our experiments additionally CR spectroscopy was applied. Here we have the following situation: The ^{12}B probes are stopped at highly symmetric sites with unperturbed cubic surroundings (see below), and their energy levels exhibit pure Zeeman splitting. The neighboring Cu nuclei, however, are subject to an additional quadrupole interaction due to an electric field gradient (EFG) caused by the B impurity. Just the presence of this additional interaction makes it possible

that for certain finite B_0 values the required energy for a $|\Delta m| = 1$ transition is equal for both spins, i.e., a “flip” of the ^{12}B spin can energetically be balanced by a “flop” of a neighboring ^{63}Cu or ^{65}Cu spin. These B_0 values are determined by magnitude and orientation of the induced EFG's and therefore depend sensitively on the probes' lattice sites and on the crystal orientation with respect to \mathbf{B}_0 . The necessary spin coupling for these flip-flops is provided by the mutual dipole-dipole interaction (DDI). From a comparison of measured and calculated CR-dip positions an unambiguous determination of the lattice location is possible. Further, the line shape of a CR dip is affected by diffusive motion. The full width at half maximum (FWHM) ΔB_0 of a CR resonance is given by [10]

$$\Delta B_0 = S\sqrt{(1/\tau_B + 1/\tau_c)^2 + 4\omega_{\text{DD}}^2}, \quad (1)$$

where ω_{DD} is the DDI matrix element in angular frequency units and the prefactor S is completely determined by known parameters of the spin Hamiltonian. The diffusional correlation time τ_c , the mean time between two successive jumps of ^{12}B , limits the time of coherent interaction for a given set of spins. If the jump rate $w = 1/\tau_c$ becomes much larger than the matrix element a lifetime broadening of the resonance takes place and eventually it vanishes [13]. More details of the theoretical treatment of CR are given in Refs. [10,12].

The essential experimental information on B in Cu after implantation is compiled in Fig. 1 where NMR spectra from McDonald and McNab [9] are shown together with selected CR data (partly from Ref. [10]) for various temperatures. The interpretation of the line shapes and positions in both types of spectra is as follows. (1) At $T = 300$ K all probes end up in unperturbed octahedral interstitial sites. This was argued already from a dipolar linewidth analysis in Ref. [9] but the first unambiguous site identification came from orientation dependent CR measurements [10]. The CR data also tell us that *only* interstitial boron (B_i) exists at this temperature. (2) B_i is essentially immobile at $T = 300$ K. Its mean occupation time at an individual position is long enough to sense the local DDI leading to inhomogeneously broadened NMR spectra and narrow CR lines. (3) At about $T = 370$ K B_i starts to diffuse. The NMR line narrows, the CR line broadens homogeneously due to the limited interaction time for an individual B_i -Cu pair. Apart from a shift of the line position due to the temperature dependence of the impurity induced EFG, which is the subject of a different paper [14], the CR pattern remains unchanged. This proves that we are still observing the same defect B_i . (4) From about $T = 400$ K on, part of the B becomes substitutional. Once again, the site was first concluded from dipolar linewidth analysis [9] and later confirmed by CR studies [10]. The transition is best seen in the CR data [Fig. 1(b)] where a new resonance emerges at $T = 400$ K. From the complete CR analysis in Ref. [10]

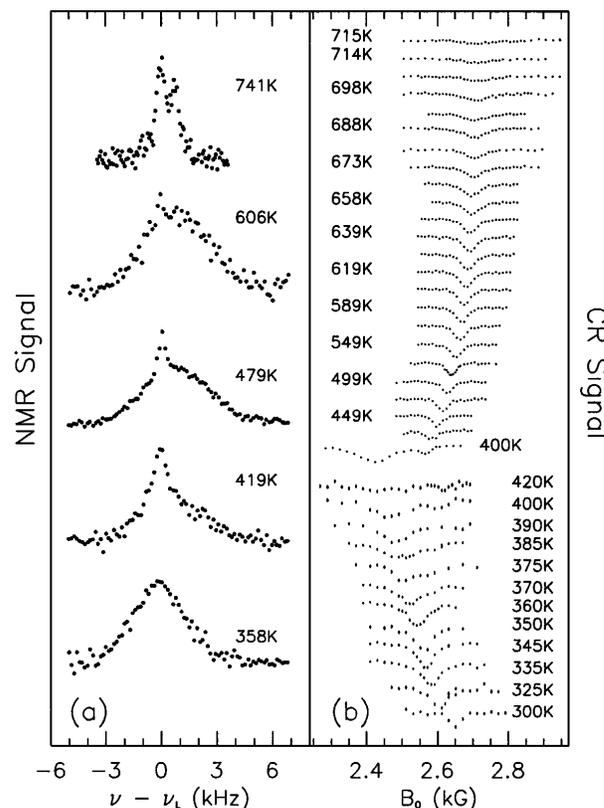


FIG. 1. NMR (a) and CR spectra (b) of ^{12}B in single-crystalline Cu at various temperatures. (a) Polarization change vs irradiated frequency (relative to the Larmor frequency ν_L), measured by R. E. McDonald and T. K. McNab [9] at $B_0 = 5.0$ kG with $\langle 111 \rangle \parallel \mathbf{B}_0$. (b) ^{12}B polarization vs B_0 for $(110) \parallel \mathbf{B}_0$. The data for $T = 300$ – 420 K have been measured previously [10] in a different single crystal. The slightly different resonance positions in both runs are due to different crystal alignment of only a few degrees. The resonance observed below $T = 400$ K is due to interstitial B, the one above 400 K is caused by substitutional B. See text for further explanations.

we know that this particular resonance corresponds to B_s interacting only with a neighboring ^{63}Cu nucleus with the probe-host vector parallel to \mathbf{B}_0 . (5) From $T = 400$ K to about $T = 600$ K we have coexistence of diffusing B_i and immobile B_s . While in the CR the B_i signal has disappeared since the DDI has been decoupled by the rapid diffusion, it is still clearly present in the NMR data. (6) Above about $T = 600$ K also the DDI of B_s gets averaged out: The NMR line of B_s narrows, the CR resonance broadens and eventually disappears.

The partial $B_i \rightarrow B_s$ conversion above $T = 400$ K can be caused only by the encounter of a mobile B_i with a copper vacancy V_{Cu} from the implantation cascade: $B_i + V_{\text{Cu}} \rightarrow B_s$. Any alternative process, like the kick-out of a regular Cu atom or recombination with a thermal V_{Cu} can be excluded since these reactions would lead to a complete rather than a partial conversion $B_i \rightarrow B_s$. The NMR spectra show that during their diffusive walk only a certain fraction of the B_i encounters a self-made V_{Cu} . This picture

is in accordance with the known thermodynamical properties of V_{Cu} . With $H_V^F = 1.28$ eV and $S_V^F = 1.6k_B$ [4] for the enthalpy and entropy, respectively, of V_{Cu} formation, we get $c_V^{\text{th}} = \exp(S_V^F/k_B - H_V^F/k_B T) = 3.7 \times 10^{-16}$ for the thermal concentration of V_{Cu} at $T = 400$ K. Clearly this is far too low to account for any observable effect.

Figure 2 shows the homogeneous widths (FWHM) of the B_s -CR resonance of Fig. 1(b) vs temperature. These homogeneous parts of the linewidths were obtained by deconvoluting the measured widths into homogeneous and fixed inhomogeneous broadenings, the latter ones known from the NMR linewidths. As stated in Eq. (1) the broadening of the CR lines starting at about $T = 600$ K reflects an increase in the B_s jump rate $1/\tau_c = w_s$. Included in the figure is a fit of Eq. (1) assuming a simple Arrhenius law for w_s , $w_s = w_{s0} \exp(-H^M/k_B T)$, where w_{s0} is the attempt frequency and H^M the activation enthalpy for migration. As fit parameters we obtain $w_{s0} = 10^{8.7(0.4)} \text{ s}^{-1}$, $H^M = 0.53(5)$ eV, and $\omega_{\text{DD}}/2\pi = 2584(64)$ Hz [15]. The jump rates extracted by means of Eq. (1) are presented in Fig. 2(b) together with the Arrhenius line calculated from the fit parameters. The attempt frequency extracted from our data is unusually low. For the following discussion, however, only the absolute jump rates are important and not their decomposition into w_{s0} and H^M , which is notoriously difficult if only a limited temperature range is accessible.

We now turn to the question of the microscopic diffusion mechanism. From the uppermost NMR spectrum in Fig. 1(a) we know that up to $T = 741$ K the B_i and the B_s resonances are well separated from each other. In a recent remeasurement (not shown) of that spectrum at $T = 748$ K and $B_0 = 3.5$ kG we confirmed this separation and found a frequency splitting of $\Delta\nu = 450$ Hz between both resonances. Any cross jumps $B_i \rightarrow B_s$, however, would lead to a motional averaging of that splitting provided the cross-jump rate exceeds $\pi\Delta\nu \approx$

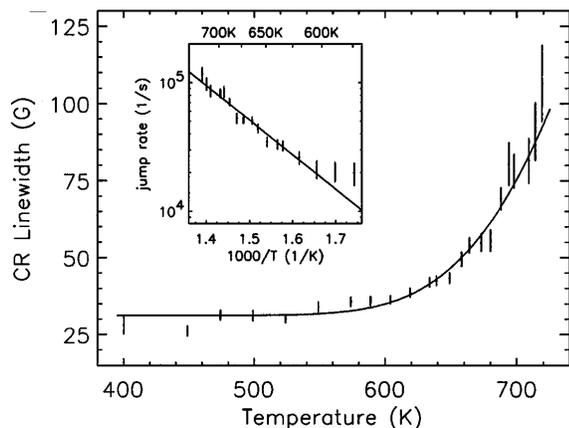


FIG. 2. Homogeneous linewidths of the B_s -CR resonances of Fig. 1(b) vs temperature together with a best fit of Eq. (1). Inset: Arrhenius plot of the extracted B_s jump rates.

1400 s^{-1} . On the other hand, we see from our activation parameters that $w_s(750 \text{ K}) = 1.4 \times 10^5 \text{ s}^{-1}$; therefore for at least 100 jumps, probably much more, the B_s diffusion takes place in a pure B_s sequence without any detectable back conversion $B_s \rightarrow B_i$: *The diffusion paths are independent of each other and do not mix*. This finding rules out, of course, the interstitialcy mechanism and dissociation $B_s \rightarrow V_{\text{Cu}} + B_i$ with subsequent kick-out $B_i \rightarrow B_s + \text{Cu}_i$ for the B_s diffusion.

Concerning V_{Cu} and Cu_i as possible vehicles for the B_s diffusion we will first consider the role of thermally created V_{Cu} and Cu_i . For two reasons we can exclude contributions of thermal V_{Cu} 's. (1) If a noticeable concentration of V_{Cu} would be present throughout the lattice the remaining B_i would completely convert to B_s , which is not the case. (2) For B_s diffusion mediated by thermal V_{Cu} 's, with concentration c_V^{th} and jump rate w_V , an upper limit for w_s would be given by $c_V^{\text{th}} w_V$ [16]. Calculating c_V^{th} as before and using $w_V = 10^{15} \text{ s}^{-1} \exp(-0.70 \text{ eV}/k_B T)$ [17] (this is also the dominating contribution to Cu self-diffusion at these temperatures) we find that the measured w_s exceeds this limit by factors of 500 ($T = 750$ K) or even 10^5 ($T = 600$ K). Regarding thermal Cu_i 's the situation is even clearer since up to the melting point their thermal concentration c_i^{th} is immeasurably small in metals (see, e.g., preface of Ref. [4]). For illustration we can take the formation enthalpy H_i^F of Cu_i as the difference of enthalpies for Frenkel pair and V_{Cu} formation, $H_i^F = H_{\text{FP}}^F - H_V^F = (4.1 - 1.28)$ eV [4], to estimate $c_i^{\text{th}} = \exp(-2.82 \text{ eV}/k_B T) = 10^{-19}$ at $T = 750$ K. We therefore conclude that B_s diffusion cannot depend on thermally created V_{Cu} 's or Cu_i 's.

Let us now assume that an athermally created defect D , either V_{Cu} or Cu_i , from the implantation cascade mediates the B_s diffusion. By use of the Monte Carlo code TRIM [18] we obtain a number of about 1000 Frenkel pairs that each implantation event of a ^{12}B nucleus initially creates under our experimental conditions. This number is substantially reduced, however, by athermal defect reactions like recombination and agglomeration, and we end up with only about 50 to 100 so-called freely migrating defects [19–21]. Comparing this figure with $w_s(750 \text{ K}) = 1.4 \times 10^5 \text{ s}^{-1}$, i.e., 4000 jumps per lifetime τ_β , we see that a single D would have to initiate many B_s jumps, which implies the formation of a somehow bound defect complex $B_s \cdot D$. Now, any nonrotating such complex would necessarily go along with an EFG at the B_s because of the lowered symmetry. Such an EFG, however, would result in a quadrupole splitting of typically 100 kHz in the NMR spectra and is clearly not in accordance with the observed narrow Larmor resonances of Fig. 1(a). An always rapidly reorienting $B_s \cdot D$ complex is also impossible, on the other hand. A reorientation of $B_s \cdot D$, rapid enough to motionally average the quadrupole interaction, would *a fortiori* decouple the much weaker DDI.

This process would therefore not broaden the CR lines but rather would terminate any CR at once. While we have worked out by now that static DDI and motionally decoupled quadrupole interaction mutually exclude each other, suspicious minds might still think of an initially isolated B_s , at rest and with cubic symmetry, which suddenly traps a D and immediately starts rapid motion. The NMR signature, however, of this scenario would be a broadened NMR, from the initial B_s state with DDI, plus a motionally averaged needle-like resonance from the final $B_s \cdot D$ state. At $T = 480$ K, for instance, we necessarily had to see both these B_s structures (plus the B_i signal) in the NMR, which clearly is not the case in Fig. 1(a). This rules out the last remaining possibility how an intrinsic defect D from the implantation damage could be involved in the B_s diffusion process. We would like to emphasize that the arguments in this paragraph equally exclude all models where unknown residual impurities in the Cu crystals are brought into play.

In summary, we have shown that no intrinsic defect like V_{Cu} or Cu_i , neither thermally nor athermally created, can serve as vehicle for the diffusion of B_s in Cu. By exclusion of all alternatives we have to conclude that the B_s migration takes place via direct exchange of B and Cu atoms.

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- [17] Both numerical values are from [4], the attempt frequency is calculated from the pre-exponential factor of the diffusion constant $D_{0,1V} = (1-1.6) \times 10^{-5} \text{ m}^2/\text{s}$.
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