Vibrational model for the direct-exchange diffusion of substitutional B in Cu

H.-J. Stöckmann, K.-H. Ergezinger, M. Füllgrabe, B. Ittermann, F. Kroll, and D. Peters

Fachbereich Physik und Wissenschaftliches Zentrum für Materialforschung der Philipps-Universität Marburg, D-35032 Marburg,

Germany

Recently it was shown that substitutional B impurities in Cu metal diffuse via a direct-exchange mechanism. In this paper a model for this mechanism is proposed. From the temperature dependence of the electric field gradient produced by the B atom at its nearest Cu neighbors it is concluded that the local vibration of the B atom within its cage of Cu neighbors triggers the direct-exchange mechanism.

The basic diffusion mechanisms for impurities or host atoms in crystalline lattices are (i) the vacancy mechanism where a substitutional atom jumps into a neighboring vacancy, (ii) the interstitial mechanism where an interstitial atom moves between interstitial sites, and (iii) the interstialcy mechanism where an interstitial atom takes the site of a substitutional one by pushing it into the interstitial lattice.[1] In contrast to these well-established scenarios information on the direct-exchange mechanism, where two neighboring atoms change their sites, either directly or in a ring process, is still scarce.[2] To the best of our knowledge up to now the only experimental verification of this process has been achieved for the case of diluted substitutional B atoms in copper metal.[3]

It is the aim of this paper to give a simple physical explanation of these findings. We shall see that a local vibration of the light B impurity triggers the site exchange between the B and one of the neighboring Cu atoms. This direct exchange is in contrast to the ring mechanisms discussed in Ref. 2. Since the argument of the present paper is applicable whenever a light impurity takes a substitutional site, it is probable that the scenario found for B in copper holds for a large number of other systems as well.

Let us start with a short recapitulation of the essential results of our previous work. Radioactive spin-polarized [12]B, produced in a nuclear reaction, was implanted into single-crystalline copper and studied by nuclear magnetic resonance and cross relaxation by monitoring the asymmetric β-decay radiation of [12]B. For details readers should consult the original paper.[3] The main result of the work was the following: In the temperature range of 400–750 K there are two B species, an interstitial and a substitutional one. Both of them diffuse independently on their respective lattices; there are no exchange jumps in between. From these findings the interstialcy mechanism is excluded. But for substitutional boron, the vacancy mechanism can be excluded as well, since the number of thermally activated vacancies in the studied temperature range is by far too small to explain the observed jump rates. The direct B-Cu exchange mechanism thus remains the only explanation for the diffusion of substitutional boron.

From cross-relaxation measurements between substitutional B and its Cu neighbors the electric field gradient (EFG) produced by the B impurity at the nearest Cu neighbor was determined.[4-6] For the following discussion one of the Cu neighbors in the bottom plane of the surrounding cube is selected as a representative (see Fig. 1). From symmetry considerations alone it is obvious that the main axes of the EFG tensor are oriented along the crystalline [101], [010], and [10$\bar{1}$] axes, and that there should be an asymmetry parameter $\eta \neq 0$. From the experiment it could be concluded only that either the largest EFG component points along the [101] axis, and the smallest one along the [10$\bar{1}$] axis, or vice versa. The second alternative is not plausible for a charged impurity, however. We therefore adopt the notation $\tilde{x}$, $\tilde{y}$, and $\tilde{z}$ for the [10$\bar{1}$], [010], and [101] axes, respectively, to be in accordance with the usual EFG conventions. The crystalline main axes are denoted by x, y, and z.

As usual, we introduce the notation $V_{\tilde{z}\tilde{z}} = eq$ and $\eta = (V_{\tilde{x}\tilde{x}} - V_{\tilde{y}\tilde{y}})/V_{\tilde{z}\tilde{z}}$ for the largest EFG component and the asymmetry parameter, respectively. For $T \lesssim 600$ K both q and η show a temperature dependence according to

$$q(T) = q_0[1 + 2.18(9) \times 10^{-4} T/\text{K}],$$

$$\eta(T) = \eta_0[1 - 1.09(30) \times 10^{-3} T/\text{K}], \quad (1)$$

with $e^2 q_0 Q(^{63}\text{Cu})/h = 1.737(7)$ MHz, $\eta_0 = 0.58(13)$ (Ref. 7), and $Q(^{63}\text{Cu}) = -0.211(4) \times 10^{-28}$ m^2 (Ref. 8). From Eqs. (1) we have

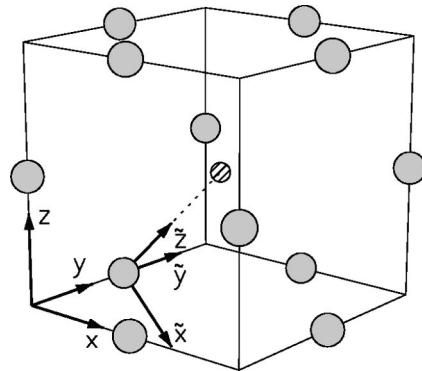$$\frac{1}{\eta_0} \frac{d\eta}{dT} = -5.2(1.5) \frac{1}{q_0} \frac{dq}{dT}. \quad (2)$$

FIG. 1. The substitutional B atom (hatched) in a fcc lattice of Cu atoms (solid circles).

    64 224301-1

The *increase* of the electric field gradient with temperature is highly unusual. The ordinary behavior is a *decrease* with temperature. In many cases it can be well described by a $T^{3/2}$ dependence[9]

$$q(T) = q_0(1 - aT^{3/2}), \qquad (3)$$

which can be explained in terms of thermal vibrations of the lattice.[10]

The increase of the EFG with temperature will turn out to be the main key for identification of the underlying mechanism. Our working hypothesis is that again lattice vibrations are responsible for the temperature dependence of the EFG. But in contrast to Ref. 10 we assume that the only vibration of relevance is the local mode of the B atom within the cage of its surrounding Cu neighbors and that the contributions of all other vibration modes can be neglected.

We start with the static case by expanding the electrostatic potential produced by the B impurity into a multipole expansion and stopping at the quartic term:

$$V(x,y,z) = f(r) + g(r)[x^4 + y^4 + z^4 - 3(x^2y^2 + x^2z^2 + y^2z^2)], \qquad (4)$$

where $f(r)$ and $g(r)$ are arbitrary functions of $r = \sqrt{x^2 + y^2 + z^2}$. For cubic symmetry there are no further terms up to fourth order. It is obvious that the expansion can contain only even powers of the coordinates, but one might argue that there should be a quadratic term in the expansion. However, because of symmetry, such a term has to be of the form $h(r)(x^2 + y^2 + z^2)$. It is thus a function of r and can be incorporated into $f(r)$.

If the potential is generated by point charges exclusively, V has to obey the homogeneous Poisson equation $\Delta V = 0$. In the far-field region the potential can be expanded as

$$V = \sum_{lm} a_{lm} \frac{Y_{lm}(\theta, \phi)}{r^{l+1}} \qquad (5)$$

with suitably chosen coefficients a_{lm}. Comparison with Eq. (4) shows that $f(r)$ and $g(r)$ are given by

$$f(r) = \frac{a}{r}, \quad g(r) = \frac{b}{r^9}, \qquad (6)$$

where a and b are constants. But due to the presence of the B impurity, the electron density is modified as well. Therefore $V(x,y,z)$ must obey the inhomogeneous Poisson equation $\Delta V = -4\pi\rho$, where ρ is the electron density. As a consequence a and b become functions of r comprising information on the electronic screening. $a(r)$ in particular is obtained from solution of the equation $a''(r) = -r\int \rho(r, \theta, \phi)d\Omega$ where the integration is over the full solid angle. This is easily seen by inserting expansion (5) into the inhomogeneous Poisson equation and using the orthogonality of the spherical harmonics.

From Eq. (4) we get for the EFG principal axis components at the nearest-neighbor sites

$$V_{\widetilde{xx}} - V_{\widetilde{yy}} = 15R^2g, \qquad$$

$$V_{\widetilde{zz}} = \frac{2}{3}R^2f_2 - \frac{1}{6}R^6g_2 - \frac{4}{3}R^4g_1 - 3R^2g, \qquad (7)$$

where $f_0 = f(R)$ and $f_{n+1} = (1/r)f_n'|_{r=R}$. Corresponding expressions hold for g_n. Here R is the distance between the B atom and the nearest Cu neighbors.

Equation (7) holds for arbitrary functions $f(r)$ and $g(r)$, i.e., arbitrary electronic charge distributions. But for the further procedure we have to make an approximation. Let us assume for simplicity that $g(r)$ is given by an exponentially screened r^{-9} potential

$$g(r) = b\frac{e^{-\lambda r}}{r^9}, \qquad (8)$$

where λ is of the order of the reciprocal lattice constant (alternatively, we could have taken a screening function oscillating with the Fermi wavelength λ_F). The value of $g(R)$ will be changed considerably by the screening, but the *ratios* R^2g_1/g and R^4g_2/g vary only by 10%–20% if λR is changed from 0 to 2 (which should cover the complete range of admissible screening lengths). We may therefore replace in Eq. (7) these ratios by their $\lambda = 0$ values at the price of an error of about 10% for the EFG components and obtain

$$V_{\widetilde{xx}} - V_{\widetilde{yy}} = 15R^2g,$$

$$V_{\widetilde{zz}} = \frac{2}{3}R^2f_2 - \frac{15}{2}R^2g. \qquad (9)$$

Equation (9) shows that f_2 and g may be expressed in terms of eq_0 and η_0 as

$$f_2 = \frac{3}{2}\left(1 + \frac{\eta_0}{2}\right)\frac{eq_0}{R^2},$$

$$g = \frac{1}{15}\eta_0\frac{eq_0}{R^2}. \qquad (10)$$

In the next step we study the change of the electrostatic potential (4) due to a vibrational shift of the position of the B atom by replacing x, y, and z by $x - x_B$, $y - y_B$, and $z - z_B$ where $r_B = (x_B, y_B, z_B)$ is the B position. Taking only the terms linear in the the B coordinates and restricting again the multipole expansion of the potential to the two leading terms, we obtain

$$V_{\text{vib}}(x,y,z) = -\left(x_B\frac{\partial}{\partial x} + y_B\frac{\partial}{\partial y} + z_B\frac{\partial}{\partial z}\right)V(x,y,z)$$

$$= -\widetilde{f}_1(r)(xx_B + yy_B + zz_B)$$

$$+ \widetilde{g}(r)[xx_B(-4x^2 + 6y^2 + 6z^2)$$

$$+ yy_B(6x^2 - 4y^2 + 6z^2)$$

$$+ zz_B(6x^2 + 6y^2 - 4z^2)]. \qquad (11)$$

We have written $\widetilde{f}_1(r)$ and $\widetilde{g}(r)$ instead of $f_1(r)$ and $g(r)$ to allow for the fact that due to the shift of the B atom the electron density and the positions of the neighboring Cu at-

oms are changed somewhat, giving rise to a modification of the radial dependencies. The first term on the right-hand side of Eq. (11) describes the vibration of the B atom within its cage, whereas the second term takes into account a vibrational tetragonal distortion of the surroundings (in addition there may be, e.g., trigonal distortions, but again we follow the philosophy adopted throughout this paper and apply the simplest approach possible).

Calculating the electric field gradient of the vibrational part of the potential and proceeding analogously as above by replacing the ratios $r^2 \tilde{f}_3 / \tilde{f}_2$, $R^2 \tilde{g}_1 / \tilde{g}$, etc., by their $\lambda = 0$ values, we obtain

$$(V_{\text{vib}})_{\tilde{x}\tilde{x}} - (V_{\text{vib}})_{\tilde{y}\tilde{y}} = 2\tilde{f}_2 (\tilde{x}\tilde{x}_B - \tilde{y}\tilde{y}_B)$$
$$+ 30\tilde{g}(4\tilde{x}\tilde{x}_B + 4\tilde{y}\tilde{y}_B + 6\tilde{z}\tilde{z}_B),$$

$$(V_{\text{vib}})_{\tilde{z}\tilde{z}} = 4\tilde{f}_2(\tilde{x}\tilde{x}_B + \tilde{y}\tilde{y}_B - 2\tilde{z}\tilde{z}_B)$$
$$+ 30\tilde{g}(6\tilde{x}\tilde{x}_B - 9\tilde{y}\tilde{y}_B - 4\tilde{z}\tilde{z}_B), \qquad (12)$$

where now $\tilde{x}_B, \tilde{y}_B, \tilde{z}_B$ and $\tilde{x}, \tilde{y}, \tilde{z}$ denote the deviations of the B and Cu atoms from their respective equilibrium positions.

In the next step the vibrational part of the EFG has to be averaged over the B position. The calculation becomes particularly simple if we assume that all vibrational averages $\langle \tilde{x}\tilde{x}_B \rangle$, $\langle \tilde{y}\tilde{y}_B \rangle$, and $\langle \tilde{z}\tilde{z}_B \rangle$ are equal. This approximation is admittedly somewhat questionable. Since the $\tilde{x}$, $\tilde{y}$, and $\tilde{z}$ directions are inequivalent, it is improbable that the averages are exactly the same. But the mean value $(\langle \tilde{x}\tilde{x}_B \rangle + \langle \tilde{y}\tilde{y}_B \rangle + \langle \tilde{z}\tilde{z}_B \rangle)/3$ cancels out, and only the deviations from the mean value survive. For the $\tilde{g}$ terms, on the other hand, the mean values do not cancel. Taking $g/f_2 = 4\eta_0/45(2 + \eta_0)$ [see Eq. (10)] as an estimation for $\tilde{g}/\tilde{f}_2$ it seems at least probable that the $\tilde{g}$ terms will dominate the $\tilde{f}_2$ ones. Neglecting thus the $\tilde{f}_2$ contributions, we obtain for the total EFG, including static and vibrational contributions,

$$(V_{\text{tot}})_{\tilde{x}\tilde{x}} - (V_{\text{tot}})_{\tilde{y}\tilde{y}} = 15R^2 g + 420\tilde{g}\langle \tilde{z}\tilde{z}_B \rangle,$$

$$(V_{\text{tot}})_{\tilde{z}\tilde{z}} = \frac{2}{3}R^2 f_2 - \frac{15}{2}R^2 g - 210\tilde{g}\langle \tilde{z}\tilde{z}_B \rangle. \qquad (13)$$

Because of momentum conservation, the vibrational average $\langle \tilde{z}\tilde{z}_B \rangle$ is negative. Furthermore, it is proportional to T in leading order. Equation (13) thus describes qualitatively correctly the linear increase of eq with T. From Eq. (13) we obtain for the relative changes of q and η with T

$$\frac{1}{q_0}\frac{dq}{dT} = -\frac{210\tilde{g}}{eq_0}\langle \tilde{z}\tilde{z}_B \rangle$$

$$\frac{1}{\eta_0}\frac{d\eta}{dT} = \frac{420\tilde{g}}{eq_0\eta_0}\langle \tilde{z}\tilde{z}_B \rangle - \frac{1}{q_0}\frac{dq}{dT}, \qquad (14)$$
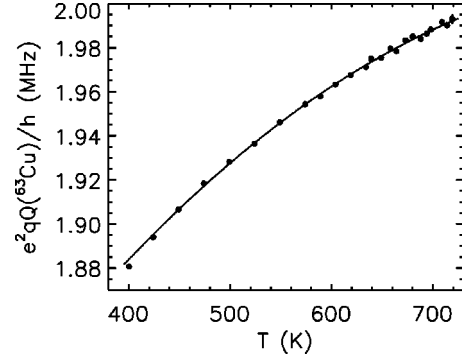
whence follows

FIG. 2. Temperature dependence of the quadrupole-coupling constant $e^2 qQ/h$ of the electric field gradient produced by B at its nearest-neighbor Cu site. The solid line is a best fit using Eq. (16).

$$\frac{1}{\eta_0}\frac{d\eta}{dT} = -\left(1 + \frac{2}{\eta_0}\right)\frac{1}{q_0}\frac{dq}{dT}. \qquad (15)$$

Inserting $\eta_0 = 0.58$ we obtain $(d\eta/dT)/\eta_0 = -4.5 (dq/dT)/q_0$, in perfect agreement with the value found in the experiment [see Eq. (2)].

For a more quantitative comparison between experiment and theory we repeated the previous EFG measurements with higher precision and over a larger temperature range. The result is shown in Fig. 2. In contrast to the earlier results[6] it is now evident that the increase of eq with temperature flattens with increasing temperature. The complete temperature dependence can be well described by

$$q(T) = q_0(1 + AT - BT^2), \qquad (16)$$

where $e^2 q_0 Q(^{63}\text{Cu})/h = 1.619(12)$ MHz, $A = 5.20(13) \times 10^{-4} \text{K}^{-1}$, and $B = 2.78(11) \times 10^{-7} \text{K}^{-2}$.

A comparison with Eq. (1) shows that the coefficient of the linear term has increased by a factor of about 2. But this is no contradiction: if the right-hand side of Eq. (16) is linearized at $T = 500$ K, we obtain a linear term in complete accordance with the earlier result.

The quadratic term in the temperature dependence of the EFG suggests that we have to go beyond the harmonic approximation to explain the experimental findings. The expansion of the mechanical potential seen by the B impurity within its cage of surrounding Cu atoms reads in the two leading orders

$$V_B(x_B, y_B, z_B) = \frac{D_0}{2}(x_B^2 + y_B^2 + z_B^2) + \frac{D_1}{2R^2}[x_B^2 + y_B^2 + z_B^2]^2$$

$$+ \frac{D_2}{2R^2}[3(x_B^2 y_B^2 + x_B^2 z_B^2 + y_B^2 z_B^2)$$

$$- (x_B^4 + y_B^4 + z_B^4)]. \qquad (17)$$

All constants D_0, D_1, and D_2 are positive provided that the repulsive part of the B-Cu interaction decreases more rapidly than r^{-1}. The second fourth-order term destroying the full rotational symmetry does not survive the vibrational average to be performed below and will therefore be dis-

carded in the following. From Eq. (17) we obtain for the equation of motion of the z_B component

$$m_B \ddot{z}_B = -D_0 z_B - 2\frac{D_1}{R^2} z_B (x_B^2 + y_B^2 + z_B^2), \qquad (18)$$

where m_B is the B mass. Corresponding equations of motion are obtained for x_B and y_B. The equations may be approximately solved by means of the ansatz

$$x_B = x_B^0 \cos \omega t, \quad y_B = y_B^0 \cos \omega t, \quad z_B = z_B^0 \cos \omega t, \qquad (19)$$

where ω still has to be determined. Replacing further x_B^2, y_B^2, and z_B^2 on the right-hand side of Eq. (18) by their time averages $(x_B^0)^2/2$, etc., we obtain

$$\omega^2 = \frac{D_0}{m_B} + \frac{D_1}{m_B R^2}[(x_B^0) + (z_B^0) + (z_B^0)^2]. \qquad (20)$$

In this approximation the fourth-order correction just leads to a modification of the vibration frequency, a fact well known from the theory of the pendulum.

The equation of motion for the z coordinate of the Cu neighbor reads

$$m_{Cu} \ddot{z} = -D_{Cu}(z - z_B), \qquad (21)$$

where D_{Cu} is the spring constant coupling the z coordinate of the Cu to the z_B coordinate of the B atom. This ansatz assumes that the neighboring Cu atom is driven by the motion of the B impurity. The fact that the vibrations of the Cu neighbors conversely modify the B vibration is ignored. This approximation is allowed in view of the fact that the mass of B is by a factor of 6 smaller than that of Cu, with the consequence that the vibration amplitude of the latter one is by about one order of magnitude smaller. With expression (19) for z_B we obtain

$$z = z_0 \cos \omega t \qquad (22)$$

as the solution, where

$$z_0 = \frac{D_{Cu}}{D_{Cu} - m_{Cu}\omega^2} z_B^0. \qquad (23)$$

Assuming that all spring constants are comparable in size, the second term in the denominator exceeds the first one by a factor of $m_{Cu}/m_B \approx 6$, justifying the approximation

$$z_0 = -\frac{D_{Cu}}{m_{Cu}\omega^2} z_B^0. \qquad (24)$$

Inserting expression (20) for ω^2 and expending the denominator we obtain up to third order in z_B^0

$$z_0 = -\frac{D_{Cu}m_B}{D_0 m_{Cu}}\{1 - \lambda_1[(x_B^0)^2 + (y_B^0)^2 + (z_B^0)^2]\}\bar{z}_B^0,$$

$$\lambda_1 = \frac{D_1}{D_0 R^2}. \qquad (25)$$

Now we are in the position to calculate the average $\langle z_0 z_B^0 \rangle$. Collecting the results from Eqs. (19)–(25) we have

$$\langle z z_B \rangle = \frac{1}{2}\langle z_0 z_B^0 \rangle$$

$$= -\frac{D_{Cu}m_B}{2D_0 m_{Cu}}[\langle (z_B^0)^2 \rangle - \lambda_1(\langle (x_B^0)^2 (z_B^0)^2 \rangle$$

$$+ \langle (y_B^0)^2 (z_B^0)^2 \rangle + \langle (z_B^0)^4 \rangle)]$$

$$= -\frac{D_{Cu}m_B}{6D_0 m_{Cu}}[\langle (r_B^0)^2 \rangle - \lambda_1 \langle (r_B^0)^4 \rangle]$$

$$= -\frac{D_{Cu}m_B}{3D_0 m_{Cu}}\left[\langle\langle (r_B)^2 \rangle\rangle - \frac{4}{3}\lambda_1\langle\langle (r_B)^4 \rangle\rangle\right], \qquad (26)$$

where $(r_B^0)^2 = \langle (x_B^0)^2 + (y_B^0)^2 + (z_B^0)^2 \rangle$ and $(r_B)^2 = (x_B)^2 + (y_B)^2 + (z_B)^2$. The inner and outer angular brackets denote averaging over amplitudes and time, respectively. In the last step we replaced $\langle (r_B^0)^2 \rangle$ and $\langle (r_B^0)^4 \rangle$ by $2\langle\langle (r_B)^2 \rangle\rangle$ and $(8/3)\langle\langle (r_B)^4 \rangle\rangle$, respectively, using $\langle \cos^2\omega t \rangle = 1/2$ and $\langle \cos^4\omega t \rangle = 3/8$. Reinterpreting the double brackets as thermal averages over the lattice vibrations, we have

$$\langle\langle (r_B)^n \rangle\rangle \qquad (27)$$

$$= \int r^n e^{-V_B(x,y,z)/k_B T} dx dy dz \bigg/ \int e^{-V_B(x,y,z)/k_B T} dx dy dz \qquad (28)$$

where $V_B(x,y,z)$ is given by Eq. (17). The calculation of the averages is straightforward and yields up to second order in $1/k_B T$

$$\langle\langle (r_B)^2 \rangle\rangle = 3\frac{k_B T}{D_0} - 30\frac{D_1}{D_0 R^2}\left(\frac{k_B T}{D_0}\right)^2,$$

$$\langle\langle (r_B)^4 \rangle\rangle = 15\left(\frac{k_B T}{D_0}\right)^2, \qquad (29)$$

whence follows from Eq. (26)

$$\langle z z_B \rangle = -\frac{D_{Cu}m_B}{D_0 m_{Cu}}\left[\frac{k_B T}{D_0} - \frac{50}{3}\frac{D_1}{D_0 R^2}\left(\frac{k_B T}{D_0}\right)^2\right]. \qquad (30)$$

Since the averages $\langle x z_B \rangle$ and $\langle z x_B \rangle$ vanish within the limits of the applied approximations, we have $\langle z z_B \rangle = \langle \widetilde{z}\widetilde{z}_B \rangle$. Inserting this result into Eq. (13) we recover the experimentally found temperature dependence (16) for $q(T)$, where

$$A = \frac{210\widetilde{g}}{e q_0}\frac{D_{Cu}m_B}{D m_{Cu}}\frac{k_B}{\widetilde{D}},$$

$$B = \frac{50}{3} \frac{D_1}{D_0 R^2} \frac{k_B}{D_0} A. \tag{31}$$

For a comparison with the experiment a number of radical approximations have to be applied. First we replace $\tilde{g}$ by $g = e q_0 \eta_0 / 15 R^2$ [see Eq. (10)]. Next, we assume again that all spring constants entering Eqs. (31) are equal. We thus get

$$A = 14 \eta_0 \frac{m_B}{m_{Cu}} \frac{k_B}{D_0 R^2},$$

$$B = \frac{50}{3} \frac{k_B}{D_0 R^2} A. \tag{32}$$

A problem poses the best value for $D_0 R^2$. It should be of the order of magnitude of the migration enthalpy E_a for substitutional B (alternatively one might express DR^2 in terms of the velocity of sound, yielding comparable results). With $E_a = 1.0$ eV (see below) we thus obtain $A = 1.3 \times 10^{-4}$ K^{-4}, which is by a factor of 4 smaller than the value found experimentally. In the same way one obtains from Eq. (32) $B/A = 1.4 \times 10^{-3}$ which has to be compared with the experimental ratio of 5.3×10^{-4}.

In view of the numerous applied approximations these correspondences have to be considered as excellent and demonstrate without doubt, in our opinion, that local B vibrations are responsible for the found temperature dependence of the EFG at the nearest-neighbor site. Of course there is no chance to get absolute values for EFG's and their temperature dependences from this heuristic approach. But all that is needed in the present context are *ratios* of different types, and ratios are much less prone to approximations as absolute values [see discussion after Eq. (8)].

The last step in the argument implies an extrapolation. Equation (25) shows that the B vibration amplitudes are larger by a factor of about m_{Cu}/m_B than those of the surrounding Cu atoms. At a given temperature the B atom has thus by far the largest probability to arrive at some saddle-point configuration, thus producing a transient Frenkel-pair configuration. This argument is corroborated by the fact that due to Eq. (29) at 600 K the nonlinear contributions to the mean-squared displacement are already of about 10%. Intuitively one may expect that occasionally the B vibration amplitudes are sufficient for it to arrive at the center of one of the faces of the surrounding cube (see Fig. 1). At this moment the chance is opened for one of the Cu atoms in the face of the cube to jump into the vacancy left by the impurity. In the subsequent step the B atom jumps into the vacant Cu position. If this picture is correct, the activation energy for the jump process should be somewhat larger than the migration energy for vacancy diffusion, $E_M = 0.70(2)$ eV, in Cu metal.[12] This is indeed the case: an analysis of the linewidths of the same cross-relaxation data used in Fig. 2 yielded a value of $E_a \approx 1.0$ eV for the migration enthalpy of the exchange process.[11] This is the main conclusion of this paper: *the direct B-Cu exchange is triggered by the local vibration of the light B impurity and does not involve ring exchanges of the type proposed by Adda et al.*[2] The same situation should hold in many similar systems. However, we still have to wait for the experiments to prove or to disprove this conjecture.

Of course, it would be useful to check the applied assumptions on the electrostatic potential produced by the presence of the B impurity by means of density functional methods. This is true in particular for the *signs* of the different contributions to the electrostatic and the mechanical potentials which cannot be obtained from symmetry considerations alone. It would be nice as well to verify the direct-exchange model presented in the last paragraph by some molecular dynamics calculation. We are confident, however, that our general conclusion will withstand these quantitative verifications.

[1] J. Philibert, *Atom Movements* (Éditions de Physique, Les Ulis, 1991).

[2] Y. Adda, N. V. Doan, and V. Pontikis, Defect Diffus. Forum **66-69**, 105 (1989).

[3] B. Ittermann, H. Ackermann, H.-J. Stöckmann, K.-H. Ergezinger, M. Heemeier, F. Kroll, F. Mai, K. Marbach, D. Peters, and G. Sulzer, Phys. Rev. Lett. **77**, 4784 (1996).

[4] E. Jäger, B. Ittermann, H.-J. Stöckmann, K. Bürkmann, B. Fischer, H.-P. Frank, G. Sulzer, H. Ackermann, and P. Heitjans, Phys. Lett. A **123**, 39 (1987).

[5] H.-J. Stöckmann, E. Jäger, G. Sulzer, B. Ittermann, H. Ackermann, E. Diehl, R. Dippel, B. Fischer, H.-P. Frank, and W. Seelinger, Hyperfine Interact. **49**, 235 (1989).

[6] G. Sulzer, B. Ittermann, E. Diehl, B. Fischer, H.-P. Frank, E. Jäger, W. Seelinger, H.-J. Stöckmann, and H. Ackermann, Z. Naturforsch., A: Phys. Sci. **49**, 354 (1994).

[7] The parameters of Eq. (1) are based on new and so far unpublished experimental data (see also Fig. 2). Within errors they agree with the values given in Ref. 6 which were based on a smaller set of spectra.

[8] P. Raghavan, At. Data Nucl. Data Tables **42** (1989).

[9] W. Witthuhn and W. Engel, in *Hyperfine Interactions of Radioactive Nuclei*, edited by J. Christiansen, Topics in Current Physics Vol. 31 (Springer, Berlin, 1983).

[10] K. Nishiyama, F. Dimling, T. Kornrumpf, and D. Riegel, Phys. Rev. Lett. **37**, 357 (1976).

[11] Previously Ref. 3, we stated a much lower value of $E_a = 0.53$ eV. The change is due to an improved theoretical understanding of the influence of the diffusion on the cross-relaxation linewidths. A full discussion of this reevaluation and its possible implications will be presented in a forthcoming publication.

[12] *Atomic Defects in Metals*, Landolt-Börnstein, New Series, Vol. III/25 (Springer, Berlin, 1991), p. 231ff.