

## Electric-field-gradient tensor for cadmium impurities in $\alpha$ -gallium

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The electric field gradient in orthorhombic gallium metal at the site of a  $^{111}\text{Cd}$  probe atom was investigated by means of the time-differential perturbed angular correlation method. By a measurement of the quadrupolar interaction in a polycrystalline sample, the quadrupole coupling constant (at 293 K)  $e^2Qq/h = 139.4(17)$  MHz and the asymmetry parameter  $\eta = 0.215(5)$  were determined. Single-crystal experiments with and without external magnetic field yielded the orientation of the electric-field-gradient tensor principal-axis system in the crystal lattice.

### I. INTRODUCTION

The electric field gradient (EFG) at a probe nucleus in a metal contains microscopic information about the local atomic environment as well as electronic structure. For some years now the EFG at impurity nuclei in noncubic metals has been the subject of investigations.<sup>1</sup> The observation that the EFG at substitutional impurity sites can be very different from that of the lattice has stimulated renewed interest in this field. Systematic trends have been observed and some understanding has been achieved. The first systematic attempt to formulate trends was made by Raghavan *et al.*<sup>2</sup> Since a larger amount of data have become available by now,<sup>1</sup> the proposed universal correlation turned out to be violated in many cases. The lattice part  $q_{\text{lat}}$  of the EFG and the electronic part  $q_{\text{el}}$  are not related to each other by a universal constant as expected from the correlation. More physical approaches have been tried by Leitz *et al.*,<sup>3</sup> Collins,<sup>4</sup> and Haas and Menningen,<sup>5</sup> relating the EFG to physical parameters such as effective charge, valence, and size of the impurity atom.

It is of importance in this respect to investigate, too, the orientation of the EFG in the crystal lattice and check to what extent it also can depend on the impurity. All existing treatments take the EFG at an impurity as proportional to that of the lattice, implying identical orientation. For the hexagonal and tetragonal metals this requirement cannot be checked, as the relation is fixed by symmetry for a substitutional probe atom. Of the simple *sp* metals only gallium offers the possibility to study this question. The pure system  $\text{GaGa}$  was investigated by Valic and Williams with nuclear quadrupole resonance (NQR), and the complete EFG tensor for that case was determined.<sup>6</sup> Earlier time-differential perturbed angular distribution (DPAD) experiments on the systems  $\text{AsGa}$  and  $\text{GeGa}$  with polycrystalline samples<sup>7,8</sup> yielded asymmetry parameters of about 0.7 in contrast to  $\eta = 0.171$  for the case of  $\text{GaGa}$ . This suggested a strong dependence of the EFG symmetry on the probe atom.

We have performed a systematic investigation of the electric-field-gradient tensors at impurity atoms in gallium. Experiments on  $\text{AsGa}$  and  $\text{GeGa}$  (Ref. 9) using single-crystal samples to obtain also the orientation of the

EFG are discussed in the subsequent paper. Experiments on further systems will be described later. In the present paper we report on the first experiment in which the complete EFG tensor in a metallic host of low symmetry is measured with the time-differential angular correlation (DPAC) technique. We have used the combined magnetic dipole and electric quadrupole interaction for  $^{111}\text{Cd}$  in gallium.

### II. THEORETICAL BACKGROUND

The elements of the EFG, a symmetric second-rank tensor, are the second derivatives of the electric potential:

$$eq_{x_i x_j} = V_{x_i x_j} = \frac{d^2 V}{dx_i dx_j} - \frac{1}{3} \delta_{ij} \Delta V.$$

Only the traceless part of the tensor contributes to the interaction. Thus the tensor is completely determined by five independent values. When it is transformed to its principal-axis system by an Euler rotation, two independent values remain. Normally the "electric field gradient"

$$eq = eq_{zz} = V_{zz}$$

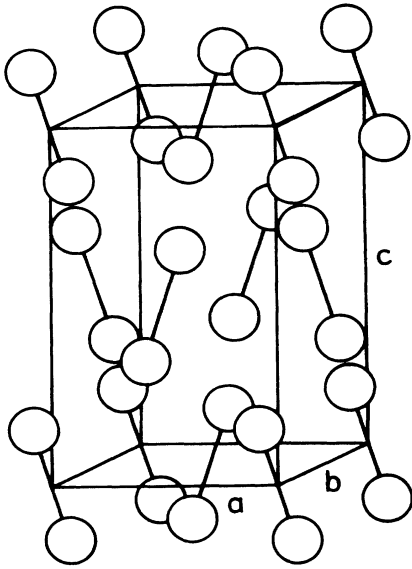
and the asymmetry parameter

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}} = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

are chosen. The principal axes are conventionally labeled so that  $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$ , and consequently  $0 \leq \eta \leq 1$ . The orientation of the tensor principal-axis system in an arbitrary coordinate system is described by the three Eulerian angles  $\alpha, \beta, \gamma$ . Together with  $q$  and  $\eta$  there are again five independent values to determine the (symmetric, traceless) electric-field-gradient tensor.

### III. THE GALLIUM CRYSTAL STRUCTURE

Gallium has an orthorhombic crystal structure (Fig. 1), somewhat related to an ideal tetragonal packing. It is therefore called pseudotetragonal. The size of the unit cell is  $a = 4.5167 \text{ \AA}$ ,  $b = 4.5107 \text{ \AA}$ ,  $c = 7.6448 \text{ \AA}$  at room

FIG. 1. The crystal structure of  $\alpha$ -gallium.

temperature. Eight atoms occupy the positions

$$\begin{aligned} &(u, 0, v), \quad (u + \frac{1}{2}, \frac{1}{2}, \bar{v}), \quad (\bar{u} + \frac{1}{2}, \frac{1}{2}, v), \\ &(\bar{u}, 0, \bar{v}), \quad (u, \frac{1}{2}, v + \frac{1}{2}), \quad (u + \frac{1}{2}, 0, \bar{v} + \frac{1}{2}), \\ &(\bar{u} + \frac{1}{2}, 0, v + \frac{1}{2}), \quad (\bar{u}, \frac{1}{2}, \bar{v} + \frac{1}{2}) \end{aligned}$$

in the unit cell, where  $u=0.0785$  and  $v=0.1525$  at room temperature. A projection of the structure on the  $a$ - $c$  plane is shown in Fig. 2. The structure may be visualized

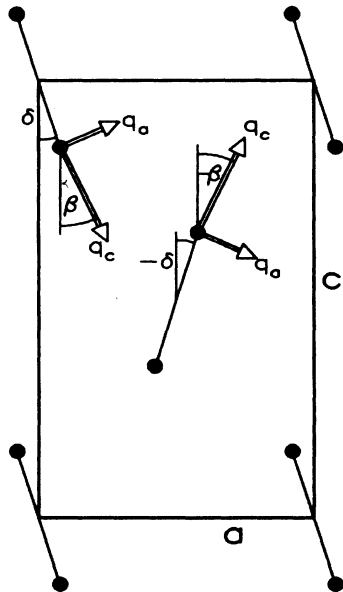


FIG. 2. Projection of the gallium structure on the  $a$ - $c$  plane with the two coexisting EFG orientations. The EFG component  $q_b$  is perpendicular to the plane.

as being composed of pairs of gallium atoms resembling diatomic molecules in the  $a$ - $c$  plane placed at every corner of the unit cell and on every face. The "molecule axis" is tilted by an angle  $\delta$  of  $16^\circ$  with respect to the  $c$  axis. The angles corresponding to the planes  $(0,0,0)$  and  $(0,0.5,0)$  have opposite sign. Each atom has one nearest neighbor at a distance of  $d_1=2.45 \text{ \AA}$  and six other neighbors in the first "sphere," each two of which at distances of  $d_2=2.70 \text{ \AA}$ ,  $d_4=2.73 \text{ \AA}$ ,  $d_3=2.79 \text{ \AA}$ . Further neighbors have distances of more than  $3.7 \text{ \AA}$ .<sup>10</sup>

The crystallographic  $b$  axis is perpendicular to a reflection plane ( $a$ - $c$ ) of the lattice. This has an important consequence for the orientation of the principal axis system of the EFG: One of the principal axes must be parallel to the crystallographic  $b$  axis ( $q_b$ ). This holds under the assumption of a substitutional site for the probe atom. To find out if  $q_{xx}$ ,  $q_{yy}$ , or  $q_{zz}$  is parallel to the  $b$  axis is equivalent to the determination of the two Eulerian angles  $\alpha, \gamma$ . The other two axes lie in the  $a$ - $c$  plane and the third angle  $\beta$  is chosen to be enclosed by the  $c$  axis and the EFG principal axis nearest to it ( $q_c$ ). Since all lattice sites are chemically equivalent, they have the same magnitude of the EFG. The Ga-Ga pairs are tilted with respect to the  $c$  axis either by an angle  $+\delta$  or  $-\delta$ . The angle  $\beta$  between the  $c$  axis and  $q_c$  will be related to  $\delta$ . Thus two sites of the same EFG but with opposite sign of  $\beta$  are present.

To determine the orientation of the EFG tensor completely one consequently has to answer three questions:

(i) Which of the three principal axes is parallel to the crystallographic  $b$  axis?

(ii) How large is the angle  $\beta$  between the  $c$  axis and the tensor principal axis nearest to it?

(iii) Does the positive or negative angle  $\beta$  belong to the positive  $\delta$ ? This cannot be decided experimentally, but can be assigned using physical arguments in the present case.

#### IV. THE DPAC PERTURBATION FUNCTION

The derivation of the perturbed angular correlation function,

$$\begin{aligned} W(\mathbf{k}_1, \mathbf{k}_2, t) = & 4\pi \sum_{k_1 k_2} \sum_{N_1 N_2} A_{k_1}(1) A_{k_2}(2) \\ & \times [(2k_1 + 1)(2k_2 + 1)]^{-1/2} \\ & \times G_{k_1 k_2}^{N_1 N_2}(t) Y_{k_1}^{*N_1}(\mathbf{k}_1) Y_{k_2}^{N_2}(\mathbf{k}_2), \end{aligned}$$

is described in detail in the literature.<sup>11</sup> A description more specific to the present problem, together with the numerical programs employed, may be obtained from the authors.<sup>12</sup> While the coefficients  $A_{k_1}(1)$  and  $A_{k_2}(2)$  are constants related to the probe nucleus, the spherical harmonics  $Y_{k_1}^{*N_1}(\mathbf{k}_1)$  and  $Y_{k_2}^{N_2}(\mathbf{k}_2)$  depend on the detector geometry, where  $\mathbf{k}_1$  and  $\mathbf{k}_2$  are the directions of the start detector and the stop detector, respectively (see Fig. 3). The perturbation function  $G_{k_1 k_2}^{N_1 N_2}(t)$  contains the informa-

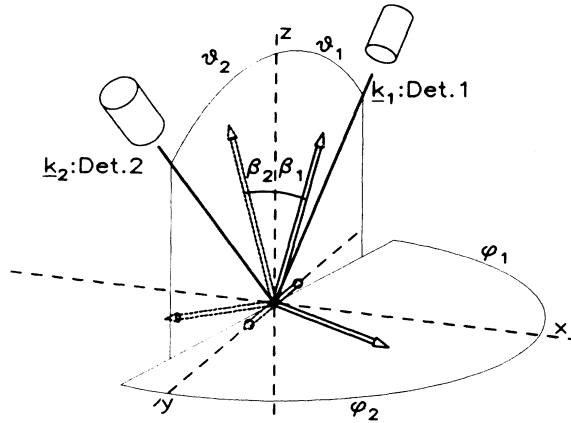


FIG. 3. Detector geometry for a typical DPAC experiment. The coordinate system of the crystal coincides with the laboratory system. The two EFG orientations are also shown.

tion about the electric field gradient and its orientation:

$$G_{k_1 k_2}^{N_1 N_2}(t) = \sum_{n, n'} S_{k_1 k_2}^{N_1 N_2}(n, n') e^{-i(i/\hbar)(E_n - E_{n'})t}$$

$E_n$  and  $E_{n'}$  are the eigenvalues of the total Hamiltonian  $H_{\text{tot}}$  describing the hyperfine interaction between the probe nucleus and the extranuclear fields. The coefficients  $S_{k_1 k_2}^{N_1 N_2}(n, n')$  have a simple relation to the eigenvectors of the total Hamiltonian of the hyperfine interaction,  $H_{\text{tot}}$ .<sup>11</sup> In the present case  $G_{k_1 k_2}^{N_1 N_2}(t)$  is an average over the two EFG sites, having positive and negative angle  $\beta$ .

To calculate the Hamiltonian for the combined magnetic dipole and electric quadrupole interaction,

$$H_{\text{tot}} = H_M + H_Q \\ = -\frac{\mu}{I} B I_z + \frac{4}{5} \sum_{i=-2}^2 (-1)^i T_i^{(2)} V_{-i}^{(2)},$$

where  $T_i^{(2)}$  are the elements of the quadrupole moment tensor in its irreducible representation,<sup>13</sup> the EFG tensor  $V_{-i}^{(2)}$  has to be expressed in the laboratory system. The direction of the magnetic field is chosen to be the  $z$  direction of the laboratory system. In nearly all experiments the crystal was oriented in such a way that the crystallographic  $b$  axis coincided with the  $y$  axis of the laboratory system, and thus the  $z$  direction lies in the  $a$ - $c$  plane. The rotation about the  $y$  axis is described by the angle  $\beta'$  between the tensor component  $q_c$  and the magnetic field. The EFG in the laboratory system in its irreducible tensor representation is

$$V_0^{(2)} = \frac{1}{8} \left( \frac{5}{\pi} \right)^{1/2} (3 \cos^2 \beta' - 1 + \eta' \sin^2 \beta') e q_c, \\ V_{\pm 1}^{(2)} = \mp \frac{1}{8} \left( \frac{30}{\pi} \right)^{1/2} \left[ \sin \beta' \left( 1 - \frac{\eta'}{3} \right) \cos \beta' \right] e q_c, \quad (1) \\ V_{\pm 2}^{(2)} = \frac{1}{16} \left( \frac{30}{\pi} \right)^{1/2} \left[ \sin^2 \beta' + \frac{\eta'}{3} (1 + \cos^2 \beta') \right] e q_c.$$

If the  $c$  axis coincides with the  $z$  direction,  $\beta'$  is identical to the Eulerian angle  $\beta$  of the orientation. If the  $a$  axis is parallel to  $z$ , the Eulerian angle is  $\beta = 90^\circ - \beta'$ . The asymmetry parameter in Eq. (1) is

$$\eta' = \frac{q_a - q_b}{q_c}.$$

Since  $q_a$ ,  $q_b$ , and  $q_c$  do not have any order in contrast to the usual convention,  $\eta'$  may be negative as well as positive, and have absolute values larger than one. Using these expressions the matrix elements of the total Hamiltonian are

$$\langle \text{Im} | H_{\text{tot}} | \text{Im} \rangle = -\hbar \omega_L m + \hbar \omega_q \frac{1}{2} [3m^2 - I(I+1)] \\ \times (3 \cos^2 \beta' - 1 + \eta' \sin^2 \beta'), \\ \langle \text{Im} | H_{\text{tot}} | \text{Im} \pm 1 \rangle = \hbar \omega_q \frac{3}{2} (2m+1) [(I \mp m)(I \pm m + 1)]^{1/2} \\ \times \sin \beta' \left[ 1 - \frac{\eta'}{3} \right] \cos \beta', \quad (2) \\ \langle \text{Im} | H_{\text{tot}} | \text{Im} \pm 2 \rangle = \hbar \omega_q \frac{3}{4} [(I \pm m + 2)(I \pm m + 1)] \\ \times (I \mp m)(I \mp m - 1)]^{1/2} \\ \times \left[ \sin^2 \beta' + \frac{\eta'}{3} (1 + \cos^2 \beta') \right],$$

where the abbreviations  $\omega_L = -\mu B / I \hbar$  and

$$\omega_q = \frac{1}{4I(2I-1)} \frac{e^2 Q q_c}{\hbar}$$

are used. In the special case  $|q_a| \leq |q_b| \leq |q_c|$ , i.e.,  $q_a = q_{xx}$ ,  $q_b = q_{yy}$ ,  $q_c = q_{zz}$ , one has  $\eta = \eta'$  and formulas (1) and (2) have their usual form (compare Ref. 14).

In the case of a pure quadrupole interaction the Hamiltonian may be expressed in the principal-axis system of the EFG. For  $\eta = 0$  it is even diagonal. Eigenvalues do not depend on  $\beta$  since no direction is distinguished by the magnetic field. Their relative spacing is fixed by the asymmetry parameter  $\eta$ . Their absolute spacing is given by the quadrupole interaction strength, i.e.,  $q_c$ . Only the coefficients  $S_{k_1 k_2}^{N_1 N_2}$  are related to the EFG orientation. To measure the orientation of the EFG principal axes in a quadrupole-interaction experiment the fitting of the effective amplitudes in the perturbed angular correlation function is required. The accuracy is therefore limited by the requirement of an absolute normalization and proper background subtraction. In some cases also ambiguities may occur. If, on the other hand, an external magnetic field is applied, the eigenvalues  $E_n, E_{n'}$  depend on the angle between the magnetic field and the EFG principal axes. The fitting parameters are now the frequencies observed in the perturbed angular correlation. If the frequencies are large compared to the inverse lifetime of the nuclear state,

$$\omega_n \gg 1/\tau_N,$$

a high precision may be achieved.

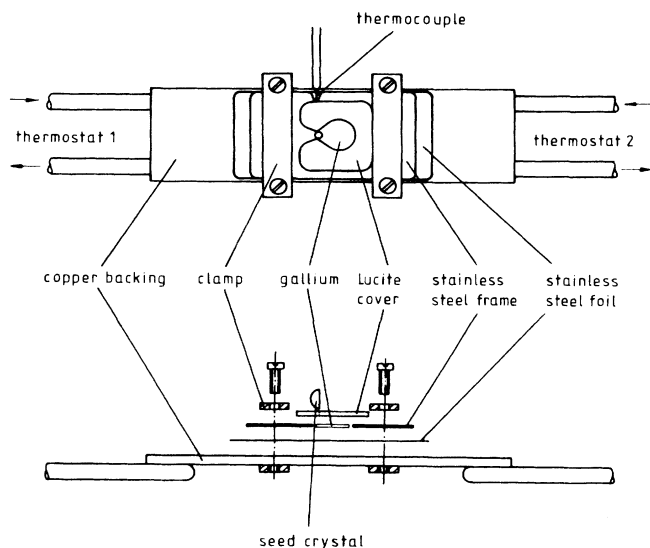


FIG. 4. The crystal-growth arrangement.

### V. EXPERIMENTAL DETAILS

The natural gallium metal (99.9999% purity) was commercially supplied. To dope our samples, gallium polycrystals and single crystals, we used carrier-free  $^{111}\text{In}$  supplied by Amersham Buchler as  $^{111}\text{InCl}_3$  in  $\text{HCl}$ . The solution was evaporated to dryness in a tungsten boat. The residue was sublimated by heating the tungsten boat to  $360^\circ\text{C}$  electrically and condensed on a cooled gallium plate of about 14-mm diameter. During this process a separation from a probable contamination of  $\text{CdCl}_2$  is achieved, as this does not evaporate below  $960^\circ\text{C}$ . In order to reduce the indium chloride and mix the molten material, the sample was held in a hydrogen atmosphere at  $500^\circ\text{C}$  for some hours. The gallium was then cleaned

in warm *aqua regia* and water and then immediately used for crystal growing to avoid oxidation. The single crystals were grown in a flat stainless-steel mold covered with a Lucite plate in a horizontal temperature gradient (Fig. 4). A seed crystal was used to achieve a defined crystal orientation. During the whole growth process the material was covered with water. The crystal samples had a thickness of 0.4 mm, a diameter of 10–12 mm, and a weight of about 180 mg.

Proper crystal orientation on a goniometer was obtained by means of backreflection Laue photographs. For the experiment in an external field a special goniometer made of Lucite was used that fitted into the 12-mm pole gap of the magnet. It allowed alignment of the crystal with an accuracy of  $0.3^\circ$  with respect to the magnetic field.

We used the well-known  $\frac{5}{2}^+$ ,  $T_{1/2}=85$  ns level of  $^{111}\text{Cd}$  in the (172–246)-keV  $\gamma$ - $\gamma$  cascade that is fed by electron capture from  $^{111}\text{In}$  with a half-life of 2.8 d. According to the spin sequence ( $\frac{7}{2} \rightarrow \frac{5}{2} \rightarrow \frac{1}{2}$ ) and the multipolarities ( $M1+2\% E2$  and  $E2$ ) only the anisotropy parameters  $A_{22}=A_2(1)A_2(2)$  and  $A_{24}=A_2(1)A_4(2)$  contribute significantly. The other terms are less than 1% of  $A_{22}$ . We have corrected  $A_{22}$  and  $A_{24}$  to account for the solid angle of the 2-in.  $\times$  5-in.-diam NaI detectors. The effective ratio of the two contributing coefficients is  $A_{24}/A_{22}=0.7$  and 1.13 for a detector-probe distance of 4 and 8 cm, respectively.

For the experiment a conventional four-detector arrangement with fast-slow coincidence was used.<sup>15</sup> To obtain the quadrupole precession spectra of a polycrystalline sample, a ratio function of the coincidence counting rates  $N(180^\circ, t)$  and  $N(90^\circ, t)$  was calculated after subtraction of a constant background:

$$R_p(t) = \frac{2}{3} \left[ \frac{N(180^\circ, t) - B_1}{\alpha(N(90^\circ, t) - B_2)} - 1 \right],$$

TABLE I. The detector geometry for the single-crystal experiments.

Run	Start detector ( $\mathbf{k}_1$ )		Stop detector ( $\mathbf{k}_2$ )		$\angle(\mathbf{k}_1, \mathbf{k}_2)$ (deg)
	$\vartheta$ (deg)	$\varphi$ (deg)	$\vartheta$ (deg)	$\varphi$ (deg)	
Pure quadrupole interaction					
1	90	0	90	180	180 (a,a)
	90	90	90	-90	180 (b,b)
	90	0	90	90	90 (a,b)
	90	90	90	0	90 (b,a)
2	90	45	90	225	180
	90	45	90	135	90
3	45	0	135	180	180
	45	0	135	0	90
Combined interaction, $\mathbf{B} \parallel \mathbf{c}$					
1	90	0	90	180	180 (a,a)
	90	90	90	-90	180 (b,b)
	90	0	90	90	90 (a,b)
	90	90	90	0	90 (b,a)

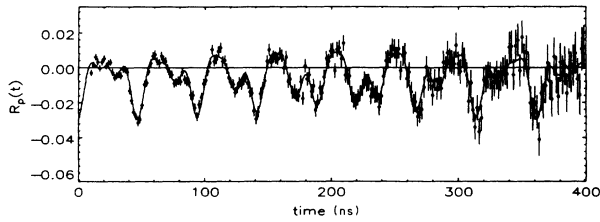


FIG. 5. Spin-precession spectrum to determine the quadrupole coupling constant and the asymmetry parameter for  $^{111}\text{Cd}$  in gallium.

where the factor  $\alpha$  accounts for the different count rates in the  $180^\circ$  and  $90^\circ$  spectra. To analyze the single-crystal experiments (see Table I), equivalent spectra were added, and after subtraction of a constant background divided by an exponential function,

$$R_s(t) = \frac{N(\mathbf{k}_1, \mathbf{k}_2, t) - B}{N_0 \exp(-t/\tau_N)} - 1.$$

## VI. RESULTS

Figure 5 shows a time spectrum from the experiment with a polycrystalline sample and the appropriate fit. Since in this case the microcrystals are randomly oriented, the perturbed angular correlation  $W(\mathbf{k}_1, \mathbf{k}_2, t)$  has to be averaged over all possible angles under the condition that the relative angle between  $\mathbf{k}_1$  and  $\mathbf{k}_2$  is constant.<sup>11</sup> Obviously this spectrum yields no information about the orientation of the EFG. However, it is possible to determine the quadrupole coupling constant  $e^2Qq/h$  and the asymmetry parameter  $\eta$  without any knowledge of the EFG orientation. In this way we obtained, at room temperature,

$$e^2Qq/h = 139.4(17) \text{ MHz}, \quad \eta = 0.215(5).$$

The experimental geometries for the single-crystal experiments are summarized in Table I. The frequencies occurring in the interaction pattern are the same as in the polycrystalline case. The amplitudes, however, depend on the EFG orientation. To answer the question of which of the EFG axes is parallel to the crystallographic  $b$  axis, two detectors aligned with the  $b$  axis were employed. Because of the axial symmetry of the setup the pattern in this case does not depend on the position of the other two axes in the  $a$ - $c$  plane and therefore not on the angle  $\beta$ . Figure 6 shows theoretical patterns for the three possible cases  $q_{xx} \parallel \mathbf{b}$ ,  $q_{yy} \parallel \mathbf{b}$ ,  $q_{zz} \parallel \mathbf{b}$  in comparison with the data obtained. Obviously only the case

$$q_{xx} \parallel \mathbf{b}$$

yields an acceptable fit. The angle  $\beta$  could be obtained roughly by measuring the quadrupole interaction with detectors placed in other directions with respect to the sample (see Table I). The orientation of the EFG is then determined by fitting the amplitudes of frequency components (Fig. 7). It should be noted, that the two inverse  $90^\circ$  spectra of run 1, ( $a, b$ ) and ( $b, a$ ), are different because

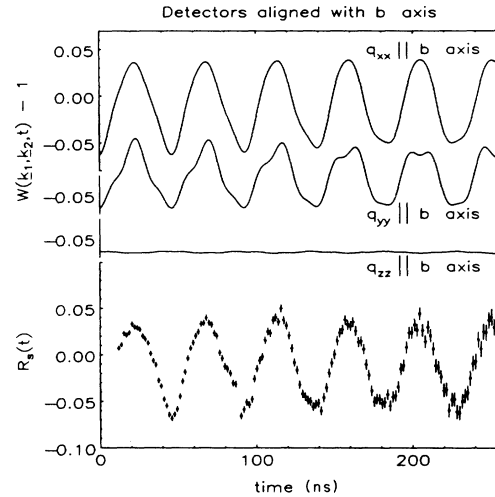


FIG. 6. Comparison of the three theoretically possible patterns for the geometry  $\mathbf{k}_1$  ( $\vartheta=90^\circ$ ,  $\varphi=90^\circ$ ) and  $\mathbf{k}_2$  ( $\vartheta=90^\circ$ ,  $\varphi=90^\circ$ ) with the experimental data.

of the influence of the  $A_{24}$  term. More precise values were obtained by measuring the combined magnetic dipole and electric quadrupole interaction in a single crystal, where the frequencies depend on the angle between the magnetic field  $\mathbf{B}$  and the EFG principal axes. Spectra were taken for the cases  $\mathbf{B} \parallel \mathbf{c}$  and  $\mathbf{B} \parallel \mathbf{a}$ . A fit of the frequencies yields an accuracy of  $1^\circ$  for the angle  $\beta$ . Figure 8 shows spectra from one such experiment using a magnetic field of  $B = 2.132 \text{ T}$ . The value obtained for the angle between the  $c$  axis and the EFG components nearest to it,  $q_{zz} = q_c$ , is

$$\beta = 24.9(10)^\circ.$$

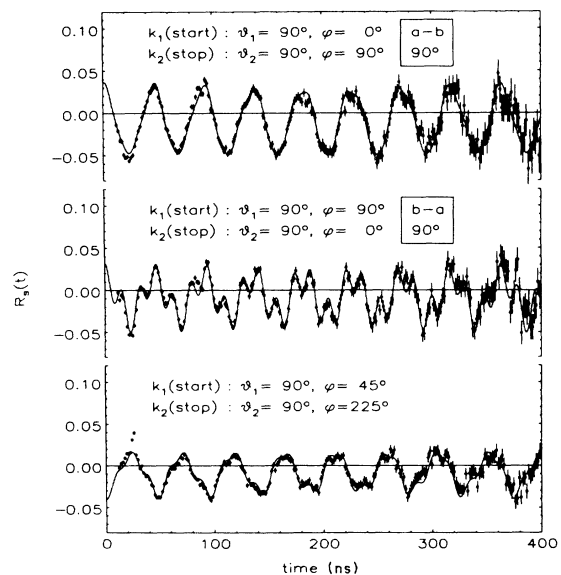


FIG. 7. Representative examples for quadrupole perturbation spectra measured at the single crystal.

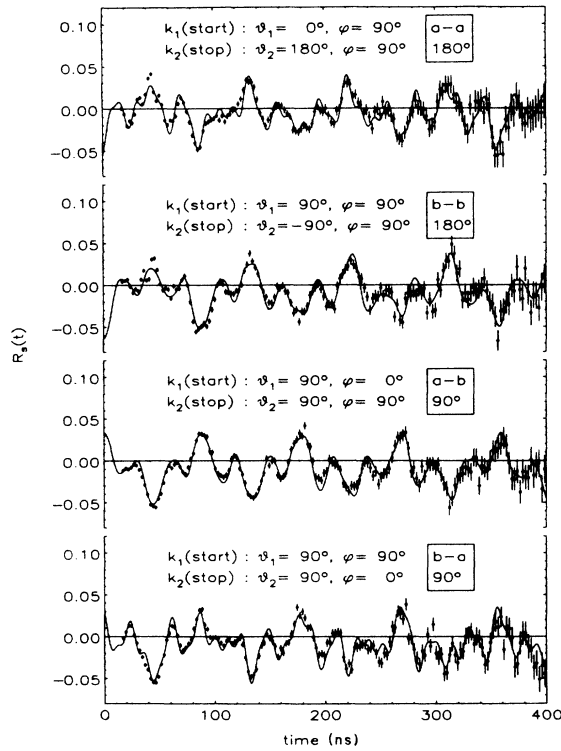


FIG. 8. Results of the combined-interaction experiment with the magnetic field  $\mathbf{B}$  parallel to the  $c$  axis for precision determination of the angle  $\beta$  between the  $c$  axis and  $q_{zz}$ .

## VII. DISCUSSION

It is very important for the following discussion to know which lattice position the  $^{111}\text{Cd}$  probe atom occupies. The radioactive parent element indium has the same valence-electron configuration as gallium. Thus it is very likely that it just replaces a gallium atom. Consequently the daughter  $^{111}\text{Cd}$  also occupies a substitutional site in the gallium lattice. This assumption is also supported by the fact that all spectra show a unique interaction which is fully described by a perturbation pattern calculated with the requirements of the symmetry of the substitutional lat-

tice site.

The magnitude of the EFG for cadmium in gallium can be calculated with use of the quadrupole moment of  $Q=0.80$  b:<sup>16</sup>  $eq_{zz}=7.2\times 10^{17}$  V/cm<sup>2</sup>. This is the largest value found for this extensively studied impurity in any noncubic metal. For the pure system  $\text{GaGa}$  the corresponding value is  $eq_{zz}=5.33\times 10^{17}$  V/cm<sup>2</sup> (Ref. 6) with  $Q=0.16$  b for  $^{69}\text{Ga}$ . In several metals for Cd and In impurities the EFG signs have been determined to be the same. Therefore also in gallium the EFG for Cd and Ga are expected to have the same sign. The orientation of the EFG for the system  $\text{CdGa}$ , however, is substantially different from the orientation in the pure system.<sup>6</sup> In both cases the largest EFG component is nearest to the crystallographic  $c$  axis including an angle of about 25° with it. This angle is not very different from the tilt angle of the Ga-Ga pairs,  $\delta=16^\circ$ . We consider this to be a proof that the positive  $\beta$  belongs to the positive  $\delta$  in both cases. The order of the remaining two EFG components, however, is opposite in the case of  $\text{CdGa}$  and  $\text{GaGa}$ , even though the absolute value of the asymmetry parameter is about the same. Neither the orientation in the pure system nor in the impurity system coincide with the orientation of the ionic EFG,  $q_{\text{ion}}$ , obtained by a lattice sum over point charges. The value we calculated is consistent with that of Lodge,<sup>17</sup> except that the axes  $q_{yy}$  and  $q_{zz}$  are interchanged. The calculation of Valic and Williams<sup>6</sup> gives a considerably different result and apparently suffers from a numerical error. Calculations using a screening potential yield a much better result for the pure system  $\alpha$ -gallium but no agreement with experiment for the  $\beta$  phase could be achieved.<sup>18</sup> The tensor parameters are summarized in Table II. For group Ib to IVa impurity atoms in simple metals it is generally found that the sign of the EFG is opposite to the one calculated from the point-charge model.<sup>2</sup> It may thus be expected that the EFG for  $\text{GaGa}$  and  $\text{CdGa}$  is negative. This would be in agreement with a simple chemical-bonding picture, where the Ga pairs are bound by higher electron density between the two atoms, leading to a negative  $q$  along this axis.

The systematic trends of  $q$  measured at different probe nuclei in the same host, e.g., Sb, show a strong variation of the EFG magnitude throughout a period of the Period-

TABLE II. Comparison of the experimental and calculated EFG tensor parameters for gallium. All parameters are valid for room temperature except those from Refs. 17 and 18, which are calculated for 2.35 and 4.2 K, respectively.

	$e^2Qq/h$ (MHz)	$\eta$	$q_b$	$q_c$	$\beta$ (deg)	$eq_{zz}$ ( $10^{17}$ V/cm <sup>2</sup> )	Ref.
$^{69}\text{Ga}$	21.6419	0.171	$q_{yy}$	$q_{zz}$	24.1	5.33	6
$^{111}\text{Cd}$	139.4(17)	0.215	$q_{xx}$	$q_{zz}$	24.9	7.2	this work
Point-charge model		0.697	$q_{xx}$	$q_{zz}$	30.0	1.1852	6
		0.972	$q_{xx}$	$q_{yy}$	34.6	1.0271	17
		0.944	$q_{xx}$	$q_{zz}$	34.5	1.043	this work
Screened potential		0.152	$q_{yy}$	$q_{zz}$	29.2		18

ic Table. This effect was assigned mainly to the change of the local electronic structure at the impurity site.<sup>5</sup> In an orthorhombic environment the variation may be different for the three tensor components  $q_{xx}, q_{yy}, q_{zz}$ , and thus account for the change of EFG symmetry.

On the other hand, the oversized Cd atom causes an elastic displacement of the neighboring Ga atoms, and therefore of the whole surrounding lattice. Even though the tensor of the elastic moduli for gallium is not very anisotropic, the displacements near the oversized impurity are expected to be very different, since the nearest-

neighbor distances vary strongly.

A quantitative discussion of these electronic and elastic effects is not possible at this time, as more experimental and theoretical data for the noncubic metals would be needed.

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