Electric-field-gradient tensor orientation for As and Ge atoms in α-gallium

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The electric-field-gradient tensor at the site of the impurity atoms ^{71,73}As and ^{69}Ge in orthorhombic gallium was measured by the time-differential perturbed angular distribution method. To analyze the spectra for the long-lived ^{73}As isomer, an autocorrelation technique was developed. The tensor orientations found are quite different from those observed for Ga lattice atoms and Cd impurities.

I. INTRODUCTION

The electric field gradient (EFG) at a nucleus in a solid can give information about the local electronic structure. For the majority of the simple metals symmetry leaves at most one tensor component to be determined. Only for gallium does the local site symmetry permit up to three components to be measured for a substitutional atom. This offers a unique opportunity to study impurities in a simple metal. The quadrupole coupling constants and asymmetry parameters for the systems ^{71}AsGa, ^{73}AsGa, and ^{69}GeGa have been determined in previous experiments.[1,2] The asymmetry parameters found for these systems ($\eta \simeq 0.7$) are considerably different from that of the pure system investigated by Valic and Williams ($\eta = 0.171$).[3] In the preceding paper, here referred to as paper I, we report on an experiment using the time-differential perturbed angular correlation (DPAC) technique to measure the electric-field-gradient tensor for ^{111}Cd in gallium.[4] It should be noted that the system CdGa shows an asymmetry parameter of about the same absolute value as the pure metal ($\eta = 0.215$). The measurement of the EFG orientation, however, showed that the EFG tensor is substantially different, since the directions of the principal axes x and y are interchanged. This finding stimulated us to start a systematic study of the gallium-impurity system.

A large variety of probe elements may be studied with the time-differential observation of the perturbed angular distribution (DPAD) following nuclear reactions. In this paper we report on the first determination of an EFG orientation using this method. For this purpose the combined magnetic dipole and electric quadrupole interaction was measured. We derived the orientation of the electric field gradient for the impurity systems AsGa and GeGa. The long lifetimes of the isomeric nuclear states allow us to measure the asymmetry and orientation of the EFG with high precision. The DPAD method is shown to be also applicable to complicated cases in quadrupole interaction studies.

A description of the properties of the orthorhombic gallium lattice was given in paper I. Since the a-c plane is a reflection plane, one of the principal axes of the EFG at a substitutional site coincides with the crystallographic b axis (q_b). When q_b is identified with one of the EFG principal axes q_{xx}, q_{yy}, or q_{zz}, only one Eulerian angle remains to be determined, i.e., the angle β between the crystallographic c axis and the EFG component nearest to it (q_c).

It is possible to measure the quadrupole coupling constant e^2Qq/h and the asymmetry parameter $\eta = (q_{xx} - q_{yy})/q_{zz}$ using a polycrystalline sample. This has been done previously.[1,2] For the full determination of the orientation of the tensor principal components, however, three further steps are necessary:

(i) The EFG component parallel to the b axis (q_b) has to be identified.

(ii) The angle β enclosed by the c axis and the EFG axis closest to it (q_c) must be determined.

(iii) The assignment of a positive or negative sign of β to one of the two equivalent sites must be made on the basis of some theoretical model if possible, because it cannot be experimentally determined.

II. THE DPAD PERTURBATION FUNCTION

The hyperfine interaction of the isomeric state is described by the same Hamiltonian as that used in paper I. The formula for DPAD has a form similar to that for DPAC:[5]

$$W(\mathbf{k}_1,\mathbf{k}_2,t) = 4\pi \sum_{k_1 k_2} \sum_{N_1 N_2} B_{k_1} A_{k_2} \times [(2k_1+1)(2k_2+1)]^{-1/2} \times G^{N_1 N_2}_{k_1 k_2}(t) Y^{*N_1}_{k_1}(\mathbf{k}_1) Y^{N_2}_{k_2}(\mathbf{k}_2) \, .$$

Here, however, $\mathbf{k}_1$ denotes the direction of the particle beam in contrast to the start-detector direction for DPAC. The factors B_{k_1} represent the alignment parameters of the nuclear state due to the populating reaction, whereas the A_{k_2} are the angular distribution coefficients of the depopulating γ transition observed. The spherical harmonics $Y^{*N_1}_{k_1}(\mathbf{k}_1)$ and $Y^{N_2}_{k_2}(\mathbf{k}_2)$ depend on the beam direction and the detector geometry, respectively. The information about the EFG is contained in the perturbation factor $G^{N_1 N_2}_{k_1 k_2}(t)$.[5] Details, particularly the treatment of combined electric and magnetic interaction, are described in paper I.

III. EXPERIMENTAL DETAILS

Isotopically enriched single crystals of ^{69}Ga and ^{71}Ga were used as targets. Enriched gallium oxide was supplied by Oak Ridge National Laboratory. It was converted to metal by electrolytic deposition. The single crystals were grown with use of a method similar to the one described in paper I. To avoid contamination of the enriched material, however, no seed crystals could be used. The crystals could thus not be grown in a specific direction. The orientations were determined by backreflection Laue photographs. The liquid gallium had to be cooled far below the melting point, as crystallization starts only below 10 °C at the colder end of the mold. Even though the crystals grow very rapidly (3–10 s), single crystals of good quality were obtained in this way.

The ^{69}Ga and ^{71}Ga targets were bombarded at the cyclotron of the Institute of Atomic Physics (IAP), Bucharest, Romania, with a pulsed 12-MeV proton and a 24-MeV α beam, respectively. The reaction ^{69}Ga $(p,n)^{69}$Ge populated the $\frac{9}{2}^+$ state ($T_{1/2}=2.8$ μs) at 398 keV.[6] The energy of the γ rays used for the angular distribution experiment were 398 keV. The 1001-keV $\frac{9}{2}^+$ state ($T_{1/2}=19.8$ ns) in ^{71}As and the 428-keV $\frac{9}{2}^+$ state ($T_{1/2}=5.6$ μs) in ^{73}As (Refs. 7 and 8) were populated via the reactions ^{69}Ga$(\alpha,2n)^{71}$As and ^{71}Ga$(\alpha,2n)^{73}$As, respectively. Gamma energies, multipolarities, and the parameters of nuclear alignment are summarized in Table I.

From the known transition multipolarities and the spin sequence $\frac{9}{2}\rightarrow\frac{5}{2}$ the ratio of the nuclear alignment parameters

$$A_{24}/A_{22}=0.6206$$

may be calculated with proper solid-angle correction, valid for all the three cases.

The targets for the ^{71}AsGa experiment were mounted on a water-cooled holder in different directions to obtain the various crystal orientations with respect to the beam-detector assembly. For the ^{73}AsGa and the ^{69}GeGa experiments specially constructed slanted goniometer holders were used which allowed precision alignment of the crystal axes.

The γ rays were observed with two 2-in.$\times$1.5-in.-diam NaI (Tl) detectors, mounted on light guides for the experiments in external magnetic fields. To record the time spectra a standard slow-fast coincidence circuit (see, e.g., Ref. 9) was used. Time spectra for lifetimes longer than the dead time of the recording electronics normally exhibit a drop in intensity immediately after the prompt peak. They then rise gradually to the normal level [dashed line in Fig. 1(a)]. The reason for this phenomenon has to be attributed to prompt events not matching the energy window chosen. The detector dead time after these prompt

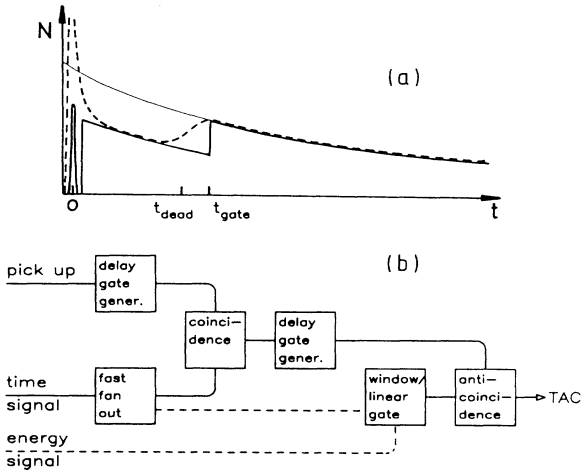

FIG. 1. (a) The detector dead time effect and (b) the cleaning system.

events reduces the probability of recording other events. After the dead time the time-to-amplitude converter is then still able to accept a stop pulse in the setup used in our experiments. To overcome the gradual change in intensity caused by the variation of the dead time, a sharp artificial dead time was introduced by an antigate triggered by prompt events [Fig. 1(b)].

The magnetic field was calibrated by measuring a DPAD spin-rotation spectrum of the same isomeric nuclear state in liquid gallium with the same experimental setup. Systematic errors, especially the time-calibration error, could be avoided in this way. The variation of the Knight shift at the melting point is expected to be negligible.

IV. DATA ANALYSIS

The extremely long lifetime of the observed isomeric states in ^{69}Ge and ^{73}As required high stability and linearity of the recording electronics. Deviations of the time spectra from exponential shape may be canceled by taking the ratio function of two simultaneously measured spectra,

$$R(t)=\frac{2}{3}\left[\frac{N_1(t)-B_1}{\alpha(N_2(t)-B_2)}-1\right].$$

Here B_1 and B_2 account for background; α adjusts the different count rates of the two detectors. A small periodic contribution due to the cyclotron frequency originates from insufficient suppression of unwanted beam pulses. It has equal phase in $N_1(t)$ and $N_2(t)$ and thus cancels in the

TABLE I. Nuclear decay parameters (see Refs. 6–8).

	$T_{1/2}$	Sequence	Multipolarity	E_γ (keV)	E_{level} (keV)	g factor
^{69}Ge	2.8 μs	$\frac{9}{2}^+\rightarrow\frac{5}{2}^-$	$M2$	398	398	−0.2224
^{71}As	19.8 ns	$\frac{9}{2}^+\rightarrow\frac{5}{2}^-$	$M2$	1001	1001	
^{73}As	5.6 μs	$\frac{9}{2}^+\rightarrow\frac{5}{2}^-$	$M2$	361	428	1.144

ratio spectrum. Since the frequencies of the perturbation function are very high compared to the inverse nuclear lifetime, the time linearity of the recording electronics is of particular importance. It was checked by recording time spectra with the direct beam from the cyclotron. From this time corrections for each channel were calculated.

A very long (~ 30 μs) time between two exciting beam pulses had to be chosen. Because of the resulting low count rate, the experiment time would have been disproportionately long to achieve good statistics in the ratio function $R(t)$. Even at low statistics, however, the time spectrum contains enough information, but distributed over a large time range. Owing to decays with short lifetimes the time range from $t=0$ to 180 ns is strongly perturbed in the direct time spectrum. The spectrum thus contains no reliable points in the first 20–30 channels.

For the analysis the autocorrelation function of the ratio $R(t)$ was therefore calculated (k=channel number) as

$$x(\tau)=\sum_k R(k)R(\tau+k) .$$

The autocorrelation reproduces essentially the periodic structure of the perturbation function and suppresses nonperiodic noise. The information of the full time spectrum is concentrated at small times. In contrast to the $R(t)$ function the autocorrelated spectrum contains reliable points already from channel 1 on. Since the autocorrelation function is an even function without any gap with a concentration of information near $\tau=0$, it is perfectly suited for Fourier transformation after multiplication by an appropriate cutoff function (see, e.g., Ref. 10). The nonlinearity of the time scale has to be corrected by interpolation before the autocorrelation procedure is performed, since a linear equidistant time scale is required.

V. RESULTS FOR ^{71}As AND ^{73}As

To obtain a rough idea of the EFG orientation, the short-lived state in ^{71}As was used to record spectra of the pure quadrupole interaction in several different crystal orientations. The beam and detector angles used are summarized in the first section of Table II. For analysis the eight spectra were divided by an exponential function after background subtraction and compared with theoretical curves according to 21 different EFG orientations covering all possible cases. The result of this analysis was:

$$q_{zz} \| \mathbf{b}, \quad \beta = 15(10)^\circ .$$

Figure 2 shows three of the measured ratio spectra with a fitted function using the orientation angle finally obtained. The fit yields a quadrupole coupling constant slightly different from that previously obtained from an experiment on a polycrystalline sample:[2]

$$^{71}\text{AsGa}: \quad e^2Qq/h = 71(5) \text{ MHz} .$$

The very-long-lived $\frac{9}{2}^+$ state in ^{73}As offers the possibility of performing a high-precision measurement of the orientation of the EFG, i.e., the angle β between the c axis and $q_c = q_{yy}$, using the combined interaction, since the orientation-dependent frequencies are very large compared to the inverse lifetime.

The crystal orientation allowed us to align the c axis with respect to the magnetic field and let the beam enter parallel to the b axis. Since the largest EFG component q_{zz} is parallel to the b axis, a high field, $B=1.80$ T, was chosen, to ensure that magnetic coupling dominates the quadrupole interaction. Consequently, the detectors were placed at $\pm 135°$ relative to the beam direction (Table II). The small misalignment of the c axis and the magnetic field, unfortunately present during this experiment, does not affect the accuracy of the β determination. This angle

TABLE II. Detector geometries in lattice coordinates.

	Beam ($\mathbf{k}_1$)		Detector ($\mathbf{k}_2$)		
Run	ϑ (deg)	φ (deg)	ϑ (deg)	φ (deg)	$\sphericalangle(\mathbf{k}_1,\mathbf{k}_2)$ (deg)
			^{71}As		
1	115	−90	65	90	180
	115	−90	90	0	90
2	107	−42	73	138	180
	107	−42	73	42	90
3	20	90	160	−90	180
	20	90	110	90	90
4	0	0	180	0	180
	0	0	90	0	90
			^{73}As		
5	90	70	90	135	65
	90	70	90	45	25
			^{69}Ge		
6	90	180	90	0	180
	90	180	90	90	90

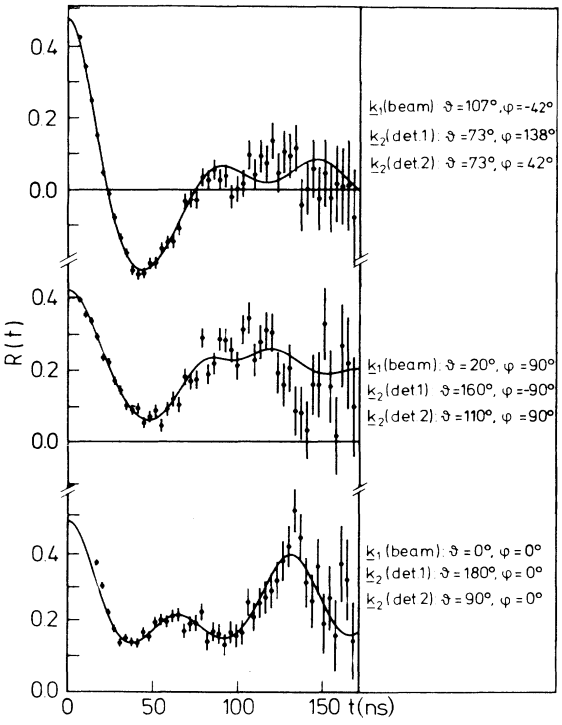

FIG. 2. Ratio spectra of the ^{71}As experiment.

is obtained as the half-difference of the angles β_1 and β_2 of the two symmetric EFG sites which is not changed by a rotation about the b axis. If the magnetic field is slightly tilted out of the a-c plane, β is also not changed to first order. Uncertainties in the direction of the incident beam (beam bending) and in the detector positions do not affect the frequencies of the perturbed angular distribution pattern which are the effective fit parameters to determine β.

A Fourier transform of the autocorrelation function of $R(t)$ for ^{73}AsGa [Fig. 3(a)] is reproduced in Fig. 4. The major frequency components show up clearly. The results of the ^{71}AsGa experiment could be verified unambiguously. The values obtained proved to be a fair starting-parameter set for the subsequent fit. The quadrupole coupling constant $e^2Qq/h=84.6$ MHz and the asymmetry parameter $\eta=0.738$ were taken from Ref. 1.

To fit the data a standard least-squares-fitting program was used.[11] The autocorrelation function of the theoretical $R(t)$ was calculated and compared with the autocorrelation function of the experimental data.

The final values of β were obtained by also adjusting e^2Qq/h and η. The resulting values obtained did not differ by more than the statistical error from the initial ones. The resulting angle between the c axis and q_{yy} is

$$\beta=11.4(1)^\circ$$

and was obtained from the angles $\beta_1=13.89(8)^\circ$ and $\beta_2=-8.92(8)^\circ$ of the two equivalent sites. The values obtained in this fit could be verified also at the original $R(t)$ spectrum [Fig. 3(b)].

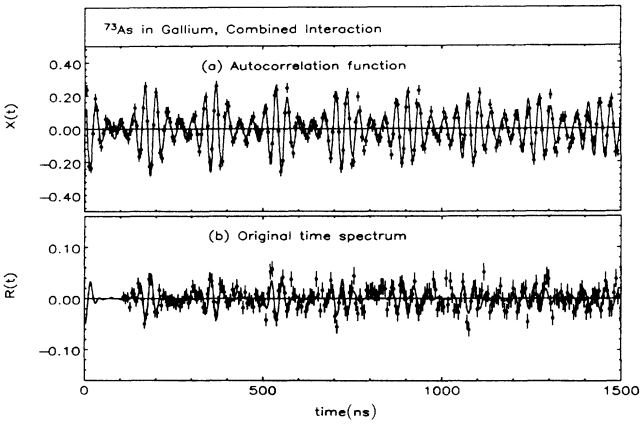

FIG. 3. (a) Autocorrelation function of (b) the ratio function of the spectrum from the ^{73}As experiment.

VI. RESULTS FOR ^{69}Ge

Contrary to the case of AsGa described above, a preliminary experiment using an isomeric state with short lifetime (e.g., ^{67}Ge $\frac{9}{2}^+$ isomer) was not performed.

The angle between the a axis and the surface normal of the isotopically pure single crystal, grown as described above, was 30°, the c axis being nearly in the plane. The a axis thus was used as the direction of beam incidence. The c axis was aligned along the magnetic field. This finally turned out to be a good choice, since the EFG component in this direction is small, yielding a large perturbation in the time spectrum even with a relatively small field of 0.6131 T in the 0°/90° detector geometry.

A Fourier transform of the autocorrelated ratio spectrum was compared with calculated frequency patterns. The parameters $e^2Qq/h=70.8$ MHz and $\eta=0.679$ were taken from Ref. 2. From this comparison

$$q_{yy}\|\mathbf{b}$$

was deduced. The angle between the c axis and $q_c=q_{zz}$ is

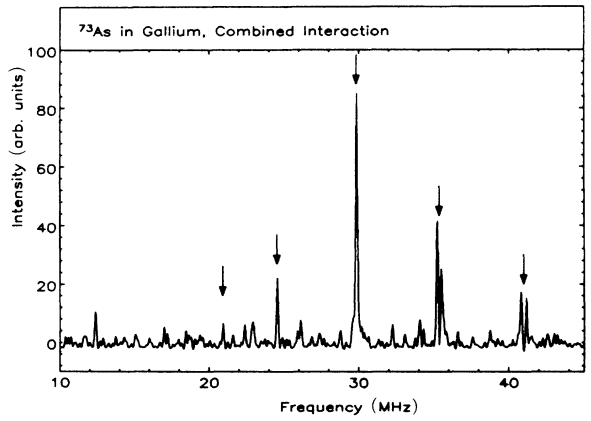

FIG. 4. Fourier transform of the ^{73}As spectrum. The major frequency components of the perturbation function are marked by arrows. The double peaks at some of the frequency components are due to the small crystal misalignment.

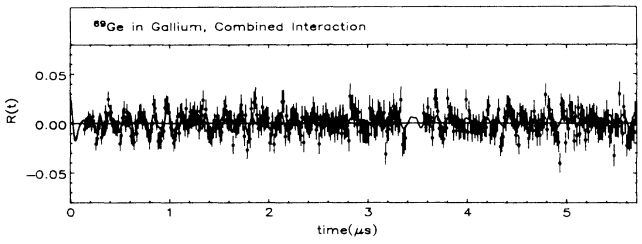

FIG. 5. Ratio spectrum of the ^{69}Ge experiment.

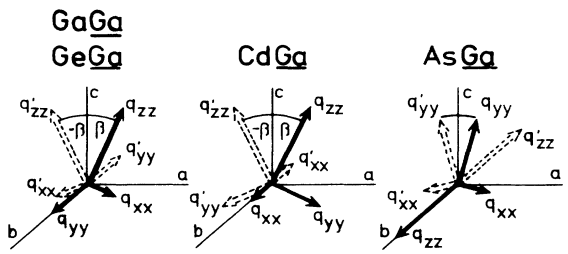

FIG. 6. EFG orientations for the probe atoms Ga, Ge, As, and Cd in α-gallium.

found to be about 25°. To obtain the final value of β, the ratio spectrum was directly fitted in this case using the least-squares-fitting procedure. The angle is

$$\beta = 25.9(5)^\circ .$$

The fitted ratio spectrum is displayed in Fig. 5.

VII. DISCUSSION

Table III summarizes the quadrupole interaction parameters determined for the impurities Ga, Ge, As, and Cd in α-gallium. Only taking into account the absolute values of η, known before the present investigations, the thought might appear that two groups of EFG symmetries are possible, suggesting two different sites in the lattice. Since the orientation of the principal-axis system varies in both groups, however, this argument is obviously not valid. In fact, all four systems investigated show a qualitatively different orientation of the EFG principal-axis system (Fig. 6). The assumption that the As or Ge ion implanted into the gallium lattice comes to rest at an interstitial position does not seem to be required. In fact, a number of in-beam investigations suggest that in virtually all cases the final position of the probe atom is a substitutional lattice site.[12,13] The substitutional site is thus also the most probable position for the probe atoms Ge and As. In both cases the observed EFG conforms to the symmetry of the substitutional site, in agreement with such an argument.

In this case it becomes possible to speculate about the sign of the angle β. For As a positive $\beta = +11.4^\circ$ may be assigned to the As-Ga pair with a positive tilt angle ($\delta = +16^\circ$) from the c axis. Similarly, for Ge, the proximity of $\beta = 25.9^\circ$ to the crystallographic angle $\delta = 16^\circ$ could be taken as evidence for a positive β. One must be aware of the uncertainty of such an assignment, however, since for the impurity atoms a much different p-bonding situation in the lattice will exist, and even the existence of close pairs is questionable. The fact that the local electronic asymmetry responsible for the EFG may be quite different from the lattice value is also strikingly exemplified by the very small EFG found for Sb in cadmium.[14]

From the measured quadrupole coupling constants the absolute value of the EFG may be calculated directly. Unfortunately, the quadrupole moments of the states employed here are not known from experiment. Using nuclear-physics arguments and some systematic trends of the EFG in group IIb and Va metals, however, one can estimate $Q(^{69}\text{Ge}) = 0.6b$ and $Q(^{73}\text{As}) = 0.7$ b. The absolute values of the electric field gradient are then

$$eq_{zz}(\text{GeGa}) = 4.9 \times 10^{17} \text{ V/cm}^2$$

and

$$eq_{zz}(\text{AsGa}) = 5.0 \times 10^{17} \text{ V/cm}^2 .$$

The results for SbCd quoted above[14] also make any assignment of the (in principle, measurable) EFG sign for the high valence probes Ge and As highly questionable. For Ge a negative q_{zz} would conform to the systematics,[15] while for As any prediction seems premature.

The measured quantities would offer an ideal testing ground for any future quantitative theory of the lattice and electronic structure about sp impurities in sp metals.

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TABLE III. Quadrupole interaction parameters for Ga, Ge, As, and Cd in gallium.

	e^2Qq/h (MHz)	η	q_b	q_c	β (deg)	eq_{zz} (10^{17} V/cm^2)	Ref.
^{69}Ga	21.6419	0.171	q_{yy}	q_{zz}	24.1	5.3	3
^{69}Ge	70.8(8)	0.679	q_{yy}	q_{zz}	30	4.9	
^{71}As	71(5)	0.738	q_{zz}	q_{yy}	11.4	5.0	
^{73}As	84.6(7)						
^{111}Cd	139.4(1.7)	0.215	q_{xx}	q_{zz}	25.0	7.2	4

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