Quadrupole Interaction of Ge Nuclei in Zn and Ga Following Nuclear Reactions

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(Received 8 January 1973)

In-beam measurements of the nuclear quadrupole interaction of the isomeric states of ^{67,69,71}Ge in the polycrystalline metallic lattices Zn and Ga demonstrate that the unperturbed quadrupole interaction pattern can be observed for several microseconds with no indication of radiation-damage effects at target temperatures near the melting point. The symmetry of the interaction in Zn suggests that the Ge recoil nuclei reach substitutional lattice sites. The interaction frequencies point to enhanced electric field gradients at the Ge nucleus.

We applied the method of time-differential perturbed angular distributions (TDPAD) following a nuclear reaction for studying the quadrupole interaction in metals. Similar experiments have been performed thus far only with the excited $\frac{5}{2}^-$ state of ^{111}Cd ($\tau = 123$ nsec) in a Cd lattice: McDonald, Lesser, and Fossan[1] observed the quadrupole interaction on Coulomb-excited ^{111}Cd nuclei recoiled into natural polycrystalline Cd; the interaction frequency they found agreed with the result of Rhagavan and Rhagavan,[2] who performed perturbed angular correlation (PAC) experiments on the same Cd state in a Cd lattice using radioactive sources. A similar in-beam experiment was done by Bleck *et al.*[3] who used the reaction ^{110}Cd(d,p) to excite the $\frac{5}{2}^-$ state in a Cd lattice. It was tempting to perform experiments with a microsecond isomer beyond the reach of a PAC experiment, in order to use the higher inherent resolution of such a state. Difficulties that can be expected are relaxation processes due to lattice defects resulting from radiation damage. On the other hand, the long lifetime proved to be a sensitive tool to elucidate such processes, as shown in an experiment with an externally applied magnetic field.[4]

In the present Letter[5] we report on the quadrupole interaction of three isomeric Ge states excited by nuclear reactions in polycrystalline Zn and Ga targets. Because of the noncubic symmetry of the host lattices, electric field gradients (EFG's) at regular lattice sites are expected. The opportunity of exciting the same nuclei as impurities in different targets may help in answering the questions of the lattice location of the recoiling Ge nuclei and in understanding the influence of the chemical difference of recoil and host atoms on the quadrupole interaction.

The first part of Table I gives a survey of the targets, the nuclear reactions employed, and the isomeric states on which the quadrupole interaction was studied. The Zn and Ga targets were bombarded with 13-MeV α particles and 6.5-MeV protons, respectively, from the 7-MV pulsed Van de Graaff at the Hahn-Meitner Institut in Berlin, to excite and align the isomeric states. The particle beam was pulsed at a 1-μsec repetition time, pulse width of ~8 nsec, for the experiments on the nanosecond isomers ^{67}Ge and ^{71}Ge. For the 2.8-μsec ^{69}Ge state the interval between two beam pulses was chosen as 8 μsec by use of an additional electrostatic deflector. The γ-ray intensity $W(\theta, t)$ of the isomeric states was observed as a function of time, t_0 given by the beam pulse hitting the target. NaI detectors appropriate for the different γ-ray energies were positioned at 0° and 90° with respect to the beam direction. In our experiments the target temper-

TABLE I. Survey of the experimental data.

Probe	I^π	E_γ (keV)	$T_{1/2}$ (nsec)	Nuclear reaction	Target	Temperature (°C)	e^2Qq/h (MHz)	η
^{67}Ge [a]	$\frac{9}{2}^+$	734	70	(α,n)	Zn (nat.)	360(15)	86.8(8)	0.0
^{69}Ge	$\frac{9}{2}^+$	398	2800	(α,n)	^{66}Zn (enr.)	360(15)	71.1(7)	0.0
				(p,n)	Ga (nat.)	−20(10)	70.8(8)	0.697(5)
^{71}Ge	$\frac{5}{2}^+$	175	84	(α,n)	Zn (nat.)	360(15)	17(3)	0.0 [b]
				(p,n)	Ga (nat.)	−20(10)	15.5(4)	0.7 [b]

[a] Previously unknown state.

[b] Parameters kept constant in the fitting procedure.

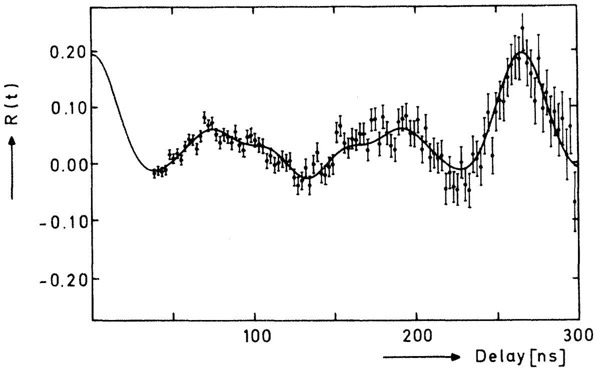

FIG. 1. TDPAD perturbation for the $\frac{9}{2}^+$ state of ^{67}Ge in polycrystalline Zn at 360°C. $R(t)$ is the modulation amplitude derived from the ratio of the time spectra at 0°. Solid curve, fit assuming an axially symmetric field gradient.

ature was ~50°K below the melting point.

The perturbed γ-ray angular distribution is given by

$$W(\theta, t) = e^{-t/\tau}[1 + A_2G_2P_2(\cos\theta) + A_4G_4P_4(\cos\theta)],$$

where the perturbation factors $G_2(t)$ and $G_4(t)$ depend on the quadrupole-interaction frequency

$$\omega_0 = [6/4I(2I-1)]e^2Qq_{zz}/\hbar,$$

with Q the nuclear quadrupole moment and q_{zz} the electric field gradient in the case of axial symmetry of the EFG. For nonaxial EFG's the interaction Hamiltonian must be diagonalized, which yields ω_0 and the asymmetry parameter

$$\eta \equiv (q_{xx} - q_{yy})/q_{zz}.$$

Figures 1 and 2 show the modulation spectra of the quadrupole interaction in Zn and Ga. The solid lines are fits with the theoretical $G_2(t)$. For the $\frac{9}{2}^+$ ^{69}Ge state following ^{66}Zn(α, n), a small but significant A_4 term must be included. The isomeric state in ^{67}Ge was not previously known. We identified it as a state with $I^\pi = \frac{9}{2}^+$ by means of the spin-sensitive quadrupole-interaction pattern. Furthermore the magnetic moment[6] has a value similar to those of the $\frac{9}{2}^+$ states in ^{69}Ge and ^{71}Ge.

In the last part of Table I we summarize the results of the least-squares-fit analysis. Obviously, the most detailed information on all relevant parameters of the interaction is obtained

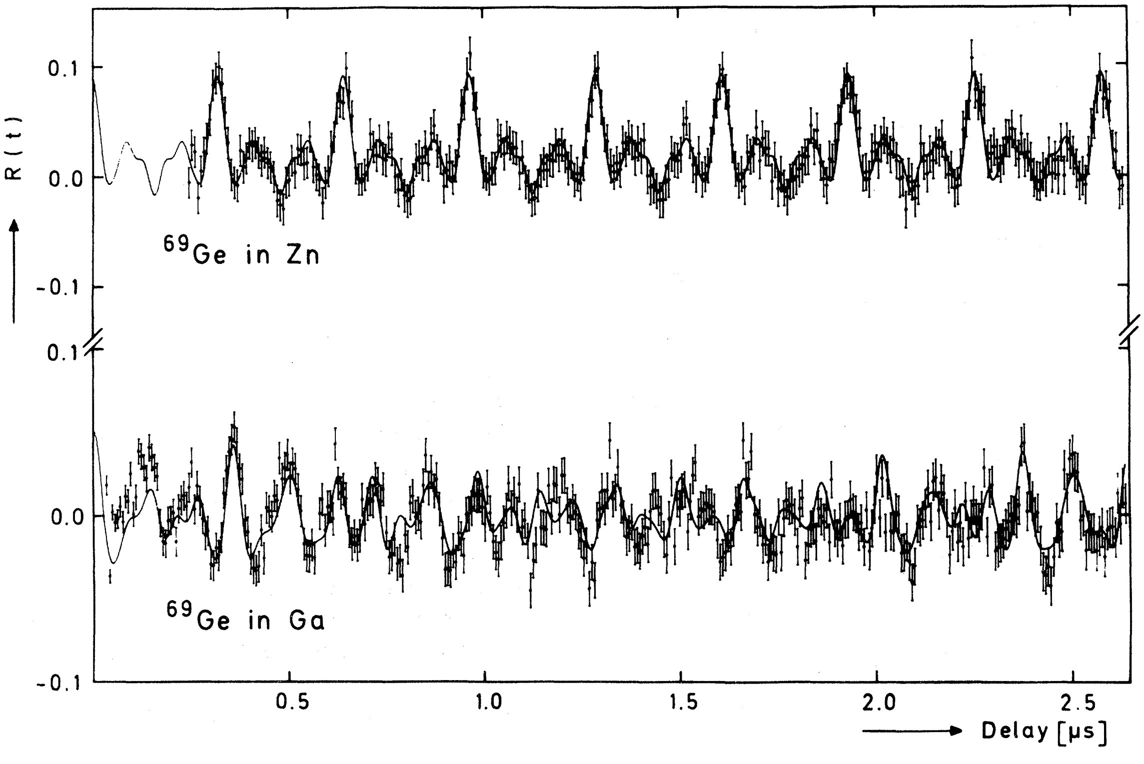

FIG. 2. TDPAD perturbation for the $\frac{9}{2}^+$ state of ^{69}Ge in polycrystalline Zn and Ga at 360 and -20°C, respectively. $R(t)$ as in Fig. 1. Solid curve for the interaction in Zn, fit assuming an axially symmetric field gradient; solid curve for Ge in Ga, fit with an asymmetry parameter $\eta = 0.697$.

from the 2.8-μsec state in ^{69}Ge. The modulation in hcp Zn could be fitted with an axially symmetric EFG, i.e., $\eta = 0$, as expected from the symmetry of the hexagonal Zn lattice. The crystal structure of GaS is orthorhombic, and a nonzero asymmetry parameter should occur; the fit yielded $\eta = 0.697$.

The experiment yields the quadrupole-interaction frequencies and the quadrupole-moment ratios, which can directly be inferred from Table I:

$$Q(^{67}\text{Ge}, \tfrac{9}{2}^{+}):Q(^{69}\text{Ge}, \tfrac{9}{2}^{+}):Q(^{71}\text{Ge}, \tfrac{5}{2}^{-}) = 1.22:1:0.219,$$

within 3% accuracy. None of these quadrupole moments or the field gradients for Ge nuclei in Zn and Ga are known. A reliable model to predict the quadrupole moments does not exist. The same holds for the field gradients for chemical impurities in metals. All we can do at present is to look at the systematics of known Q moments in this mass region. Concerning the $\frac{9}{2}^{+}$ states, the only moment at hand for comparison is $Q(^{73}\text{Ge}, \frac{9}{2}^{+}\text{g.s.})$, which is $Q = 0.17b$.[7] The $\frac{5}{2}^{-}$ state moment can be compared with $Q(^{69}\text{Ge}, \frac{5}{2}^{-}\text{g.s.})$, which is $Q = 0.028b$[8]; the ratio $Q(^{73}\text{Ge}, \frac{9}{2}^{+}):Q(^{69}\text{Ge}, \frac{5}{2}^{-})$, taken directly from the hyperfine constants b, is 1:0.153 and may be compared with the ratio 1:0.219 given above.

With the uncertainty of the Q moments in mind, we can try to understand the EFG of the Ge impurity in Zn and Ga. No experimental result concerning Zn is available in the literature for comparison. A recent TDPAD experiment[9] on the $\frac{9}{2}^{+}$ state in ^{67}Zn following the reaction $^{66}\text{Zn}(d,p)$ gives a rough estimate for the EFG in Zn at a Zn nucleus. The situation for Ga is much better. A nuclear-quadrupole-resonance experiment on a Ga single crystal provides us with temperature-dependent data on the EFG tensor in this metal. At 285°K, near the temperature of our experiment, Valic and Williams[10] obtained $q_{zz} = 6.78 \times 10^{17}$ V/cm^2. Taking the Q moment of Refs. 7 and 8, we get for Ge in Ga, $q_{zz} = 2.48 \times 10^{18}$ V/cm^2, which is more than 3 times larger and should be outside the possible uncertainty of the Q moment for the ^{69}Ge $\frac{9}{2}^{+}$ state. This points to an enhancement of the field gradient by substituting a host Ga atom by the Ge atom. The same holds qualitatively for the Zn case. The interaction frequency for the $\frac{9}{2}^{+}$ state in Zn is smaller by a factor of 2,[9] compared with the $\frac{9}{2}^{+}$ state of Ge in Zn; again the difference between the two $\frac{9}{2}^{+}$-state quadrupole moments of ^{67}Zn and ^{69}Ge is not expected to be this large.

The field gradient q at a nucleus arises from two sources: a contribution q_{ion} from the positive ions in the lattice and a contribution q_{el} due to the conduction electrons, $q = q_{\text{ion}} + q_{\text{el}}$. Whereas q_{ion} can be obtained rather accurately by summation techniques,[11] the calculation of q_{el} is by far more difficult, since it depends on the wave function of the conduction bands. In recent publications[12,13] the contribution to q_{el} is decomposed into two parts, the first arising from the distortion of the Fermi surface by the lattice potential and the consequent contribution of these Fermi electrons to q_{el}, and the second from all the band electrons below the Fermi surface. The first mechanism was shown to be important for transition metals because of the high density of states at the Fermi surface; the second proved dominant in the nontransition metals Be, Mg, and Sb. In analogy, we think this part yields the main contribution in the polyvalent metals Zn and Ga.

An additional parameter is measured by the interaction in orthorhombic Ga. The EFG of Ga in a lattice has an asymmetry parameter $\eta = 0.171$,[10] whereas we obtained $\eta = 0.697$ for Ge in Ga. The asymmetry parameter η again results from a contribution of the lattice and the conduction electrons. In Ref. 10 the contribution of the lattice η_{ion} was calculated to be $\eta_{\text{ion}} = 0.697$. The contribution of the Ga conduction electrons changes this value to $\eta = 0.171$. The same value of the measured η for Ge in Ga with η_{ion} must be considered as accidental. No theoretical treatment for this problem is at hand and to our knowledge no other experiment thus far has measured the asymmetry parameter for a chemical impurity in a nontransition metal.

From the unique field gradients we measured in these experiments and the absence of relaxation effects, we conclude that the recoil ions, which are chemical impurities in the host lattice but have almost equal mass numbers, come to rest on substitutional sites and see the unperturbed crystal environment.

We are indebted to Professor K. H. Lindenberger for his continuous interest in this work. We thank H. Bertschat *et al.* (Ref. 9) for providing us with their experimental result prior to publication.

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Similarities in the Valence Bands of Amorphous and Crystalline GeTe Determined by X-Ray Photoemission

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(Received 19 December 1972)

We have measured the valence-band density of states and the energies of the core levels of crystalline and amorphous GeTe with x-ray photoemission. The density of states of the amorphous form is found to be very similar to that of the crystal. The present results indicate that the atomic orbitals primarily determine the valence-band density of states and that these are disturbed little, even when the bonding changes significantly.

Although the details of the structure of amorphous GeTe have not been conclusively determined, it is well established that the amorphous and crystalline phases are significantly different.[1-5] The density of the amorphous form has been measured to be 5.6 ± 0.5 g/cm^3, compared with the crystalline density of 6.17 g/cm^3.[6,7] In the crystalline form, GeTe has a slightly distorted rocksalt structure in which each atom is coordinated to six neighbors of the opposite kind with a separation of 3.0 Å. In the amorphous form the coordination number is reduced to an average of about 3, with a nearest-neighbor separation of 2.7 Å.[1-5] Thus, in the amorphous form not only is the long-range order absent, but the short-range order is very different from that of the crystal. The structural data of the amorphous form are best described by a random covalent model in which Ge-Ge, Te-Te, and Ge-Te bonds are equally likely, while Ge remains fourfold coordinated and Te twofold coordinated.[3]

The change in the structure was interpreted as representing a change in the bonding from ionic in the crystal to covalent in the amorphous form.[2] The change in the zero-frequency dielectric constant, from 36 in the crystalline form to 11 in the amorphous form,[8] indicated that large changes were taking place in the bonding. Brodsky and Stiles[8] suggested that the strengthening of the bonding in the amorphous form arose from the shortening of the interatomic distances, leading to a rescaling of the parameters E_h and C, which determine the features of the band structure. Even aside from the destruction of the long-range order, one would expect the large changes in these parameters alone to modify the valence-band density of states drastically.

Compounds which crystallize in the rock-salt structure are believed to do so because of the pronounced ionic character of their bonds. If the ionicity were indeed to increase by a large amount upon crystallization, then we should expect to see large shifts in the positions of the core levels of the Ge and Te atoms in opposite directions, due to the charge transfer between the two types of atoms. X-ray-induced electron emission is the ideal tool for such investigation because differences between core levels (e.g., Ge $3d$ and the $j = \frac{5}{2}$ component of the Te $4d$ orbitals) can be measured to within ± 0.1 eV.[9] The