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Impact of magnetic field on directional crystallization in gallium

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We used nuclear magnetic resonance to study the impact of strong magnetic field on the orientation of gallium crystalline axes during crystallization from melted gallium. Directional crystallization of gallium was observed in magnetic fields of 7, 9.4 and 11.7 T by the appearance of the narrow resonance lines similar to those in single crystals. The orienting effect of the magnetic field has been demonstrated during the formation of both the stable α-Ga and the metastable β-Ga. It was shown that the crystalline a axis was directed along the magnetic field in oriented α-Ga regions. The fractions of oriented α-Ga and β-Ga increased with increasing magnetic field from 0.24 for 7 T to 0.4 for 11.7 T.

Keywords: directional solidification in magnetic field, gallium, nuclear magnetic resonance, α-Ga; β-Ga.

1. Introduction

The development of methods for producing the textured metals and metallic alloys with a specific orientation of the crystalline axes is of great practical importance for creating materials with tailored characteristics. Studies conducted to date have shown that the application of external electric and magnetic fields can have a significant effect on the microstructure and phase composition of polycrystalline samples [1]. The orienting effect of strong magnetic fields during melt crystallization was demonstrated by examples of a number of non-magnetic eutectic metallic alloys [2,3] and pure metals [4,5]. Common methods of proving the formation of an oriented phase during crystallization are X-ray diffraction and electron microscopy, the disadvantage of which is the inability to observe the texture of materials directly during formation. This raises certain doubts about the effectiveness of the influence of the magnetic field on the texture of crystallized pure metals and alloys. In papers [9–11], it was proposed to use the nuclear magnetic resonance (NMR). The NMR line frequencies depend on the temperature, the aggregate state of the material under study, and the orientation of the crystalline axes relative to the magnetic field, which makes it possible to directly detect the orienting effect of the magnetic field. Using NMR, indisputable evidence of orientational crystallization in tin [9,10] and gallium [11] in a magnetic field was obtained.

In the present study, further NMR examination of metallic gallium structure formed upon cooling of the melt in three different superconducting magnets in fields 7, 9.4 and 11.7 T were carried out. Gallium and its alloys are widely used in modern microelectronics, flexible robotics, wearable electronic devices, and medical diagnostics [12–14].

2. Sample and experiment

The sample for the study was prepared from metallic gallium of 3N purity and consisted of a ball with a diameter of 1 mm wrapped in Teflon tape. The Bruker pulse NMR-spectrometers DPX 300 (field 7 T), Avance 400 (field 9.4 T) and Avance 500 (field 11.7 T) were used to study the effect of strong magnetic field on the melt crystallization. Signals from gallium isotopes, ^{69}Ga and ^{71}Ga, were observed within the temperature range from 150 to 350 K. The rate of temperature change did not exceed 0.5 K/min and the accuracy of temperature stabilization was no worse than 0.2 K. After temperature stabilization, the sample was kept for 10 min before the start of measurements. The angular dependences of the positions of the resonance lines were studied on Avance 400 spectrometer in a field of 9.4 T.

The ^{69}Ga and ^{71}Ga gallium isotopes have similar natural abundance (60 and 40 %, respectively) and spin $I = 3/2$. Their gyromagnetic ratios γ and quadrupole moments Q are equal $\gamma_{69} = 6.44 \cdot 10^{-7}$ rad $\cdot$ T^{-1}s^{-1}, $Q_{69} = 0.168$ barn and $\gamma_{71} = 8.18 \cdot 10^{-7}$ rad $\cdot$ T^{-1}s^{-1}, $Q_{71} = 0.106$ barn. To obtain resonance gallium lines at various temperatures, the Fourier transform of the free precession signal after a 90-degree pulse was used. The NMR line shift was calculated relative to the position of the resonance line in GaAs crystal. The spin-lattice relaxation time was determined by restoring the

nuclear magnetization signal after an inversion 180-degree pulse (inversion recovery procedure).

The NMR spectra of metallic gallium differ significantly in liquid and crystalline states. The resonance lines of melted gallium are narrow Lorentzians shifted relative to the position of the lines in GaAs crystal [15]. Upon crystallization of gallium from a melt into a stable α modification, the spectra of polycrystals are strongly broadened due to the anisotropy of the quadrupole interaction and, to a lesser extent, the anisotropy of the Knight shift [16,17]. Such polycrystalline spectra are generally not registered using NMR. However, the resonance lines of both gallium isotopes in single crystals of α-Ga are the narrow Gaussian contours [18]. The frequencies of these resonance lines strongly depend on the orientation of the single crystal in the magnetic field. The above also applies to NMR spectra in the metastable β-phase formed from a supercooled melt. The strong orientation dependences of the resonance frequencies make it possible to unambiguously identify the directional ordering of the crystalline axes that occurs under the influence of an external magnetic field.

3. Results

The melting point of stable α-modification of gallium is 302.9 K. The position of the Lorentzian contour in the melt is determined mainly by isotropic Knight shift. An example of NMR line for ^{71}Ga isotope at a temperature of 314 K obtained in 9.4 T field is shown in the inset in Figure 1. Gallium is prone to supercooling, and the resonance line of supercooled gallium also has a Lorentzian shape. In this case, the integral intensity of the NMR line is proportional to the amount of melt. Figure 1 shows the temperature dependence of the integral intensity of the resonance line of ^{71}Ga isotope in the gallium melt when the sample is cooled from 314 K to 156 K, followed by heating to the initial temperature. During crystallization and melting, the integral intensity changed abruptly, and the width of the thermal hysteresis was 30 K. The NMR signal from supercooled liquid gallium disappeared at a temperature of 270.9 K. At the same temperature, two Gaussian lines significantly shifted in frequency appeared in ^{71}Ga NMR spectrum, which were observed throughout the temperature range of crystalline gallium. The insert to Figure 2 shows an example of the spectrum at 270.9 K. The line frequencies were 1940 and 220 ppm. The positions of these Gaussians are within the polycrystalline line corresponding to the central transition $+1/2 \leftrightarrow -1/2$ and estimated from the quadrupole constants for α-Ga found in [16]. For both isotopes of gallium, the total integral intensity of Gaussians was about 0.15 of the integral intensity of the NMR line of melted gallium. The intensity of the Gaussians increased slightly with decreasing temperature in accordance with Curie's law. When the sample was heated, the Lorentzian signal from liquid gallium appeared at a temperature of 303 K simultaneously with the disappearance of two
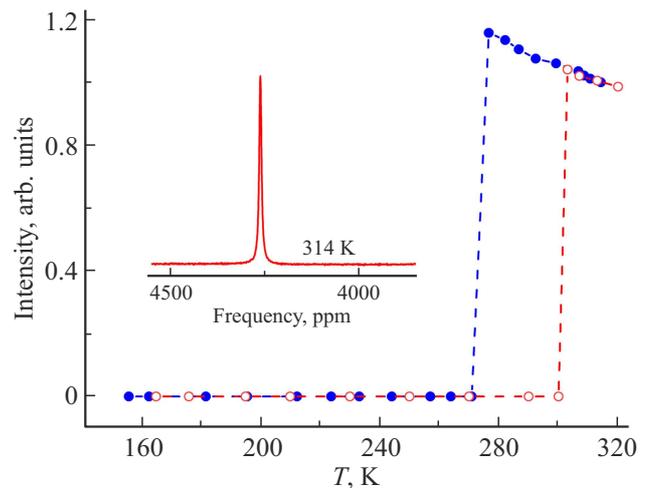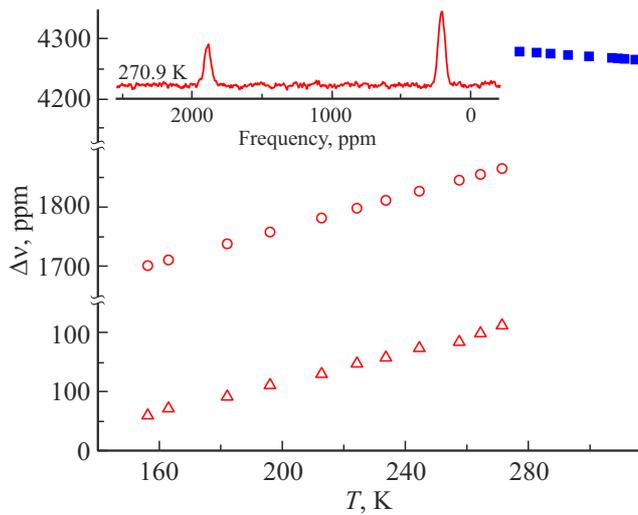

Figure 1. Temperature dependence of the integral intensity of NMR signal of ^{71}Ga for melted gallium during cooling (blue filled circles) and heating (red empty circles). Dashed lines are shown for clarity. In the insert: NMR line of ^{71}Ga isotope in the melted gallium at a temperature of 314 K.

Gaussians. These results confirm the assumption made in [11] that Gaussians correspond to the central transition $+1/2 \leftrightarrow -1/2$ in the oriented part of α-Ga. Satellite transitions $\pm1/2 \leftrightarrow \pm3/2$ were not observed, as they are strongly broadened due to the quadrupole interaction. Since the integral intensity of NMR signal in the gallium melt corresponds to all resonance transitions, we can estimate the proportion d of the oriented gallium $d \approx 0.15/0.4 = 0.375$, taking into account that for spin $I = 3/2$, the central transition accounts for 0.4 NMR signal intensity [19]. The formation of oriented α-Ga during crystallization in a magnetic field was reproduced under the temperature conditions described above. The proportion of oriented gallium from the total amount of crystalline gallium was close to 1/3.

Figure 2 shows the temperature dependences of the frequency shifts of Lorentzian line from the gallium melt, as well as two Gaussian lines corresponding to oriented crystalline gallium, during sample cooling. In contrast to the temperature dependence of the Knight isotropic shift in a melt, the shifts of Gaussian lines decline with decreasing temperature.

The orientation crystallization of metals and alloys in a strong magnetic field is explained by the formation of crystalline nuclei upon cooling, the crystalline axes of which are oriented in accordance with the condition of minimizing magnetic energy (see [2,3] and references therein). The reproducibility of NMR spectra in repeated temperature cycles is consistent with this directed crystallization mechanism for gallium. To prove the existence of a preferential orientation of the nuclei crystalline axes in a strong magnetic field, the sample was cooled from 314 K to 270.9 K, when the signal from the melt disappeared, and two lines of oriented α-Ga emerged (Figure 3, a). The sample was then

Figure 2. Temperature dependences of the frequency shifts of NMR lines of ^{71}Ga for melted gallium (blue squares) and oriented α-Ga (red circles and triangles). In the insert — NMR spectrum of ^{71}Ga for the oriented α-Ga at a temperature of 270.9 K.

rotated by an angle of 25° clockwise around a horizontal axis perpendicular to the direction of the magnetic field. The spectrum with frequency-shifted lines is shown in Figure 3, *b*. After heating to 314 K, the lines corresponding to the oriented gallium disappeared, indicating complete melting. After repeated cooling down to 270.9 K the lines emerged again (Figure 3, *c*). Their positions were close to the positions of lines during the first cooling as shown in Figure 3, *a*. Thus, melted gallium does not retain memory of the direction of the crystalline axes, and upon repeated cooling, an energetically favorable orientation in a magnetic field is reproduced for the crystalline phase.

The structure of crystallized gallium can change with varying temperature cycle limits. In paper [20], it was demonstrated that heating gallium to higher temperatures enhances supercooling of the melt and leads to the formation of a metastable β-Ga. To identify potential orientational crystallization of β-phase the sample of gallium was heated up to 340 K and then cooled. The crystallization took place at 257 K (in contrast to 270.9 K in the previous temperature cycles). After cooling down to 233 K the sample was heated. Complete melting was observed at 267 K, which corresponds to melting of β-Ga. The integral intensity of ^{71}Ga signal from melt is shown in Figure 4. Below 257 K during cooling and 267 K during heating, a single narrow NMR line associated with oriented β-Ga was registered (an example at 257 K is shown in the insert to Figure 4). The position of this line is close to the frequency of the line for liquid gallium, which reflects the similarity in structures of β-Ga and the melt [21]. The signal intensity was weakly dependent on the temperature. Based on measuring the intensity of NMR signals in the melt and oriented β-Ga, the fraction of oriented β-Ga was estimated to be 1/3, as was the fraction of oriented α-Ga.

When the sample was cooled down below 230 K the signal from the oriented β-Ga vanished. No signals from oriented solid gallium were observed below 150 K and upon subsequent heating to the melting point of α-Ga. The narrow line from the melt emerged at 303 K. This result indicates the recrystallization of metastable β-Ga into stable α-Ga, which is consistent with studies of bulk gallium polymorphism [20]. During the polymorphic phase transition, the orientational order in β-Ga was destroyed, and the order corresponding to the energetically favorable orientation of α-Ga, as expected, was not established. The
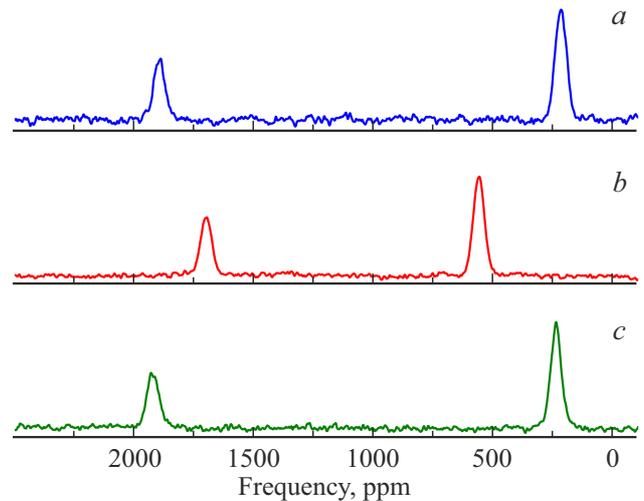

Figure 3. NMR spectra of ^{71}Ga at a temperature of 270.9 K for α-Ga right after crystallization (*a*), after the sample rotation by 25° (*b*), after the sample heating up to 314 K and further cooling to 270.9 K (*c*).
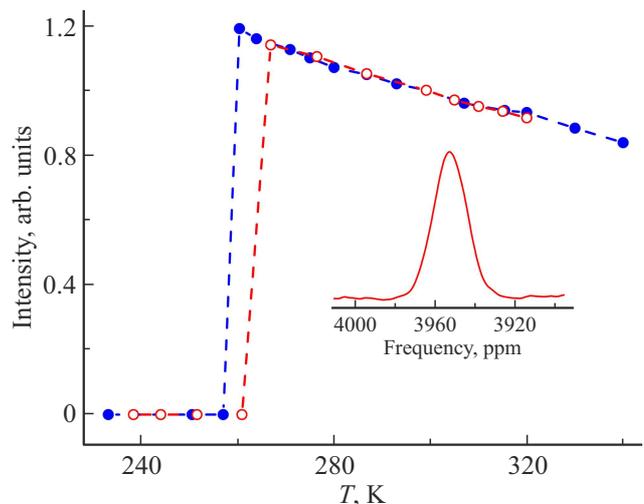
Figure 4. Integral intensity of NMR signal of ^{71}Ga for melted gallium during the sample cooling from temperature 340 K to 233 K (blue filled circles) and subsequent heating (red empty circles). Dashed lines are shown for clarity. In the insert — NMR line of ^{71}Ga for the oriented β-Ga at 257 K.
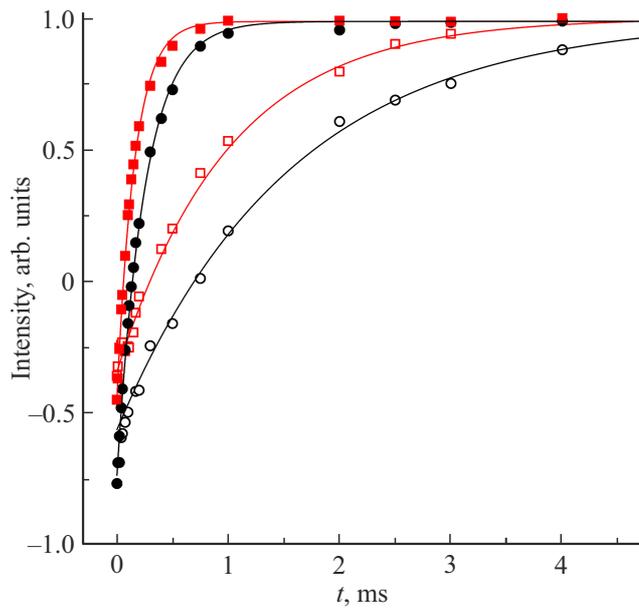
Figure 5. The NMR lines recovery curves after inversion at a temperature of 295 K for the oriented α-phase and at a temperature of 260 K for the oriented β-phase. t — the time between the inverting and 90-degree pulses. Squares — ^{69}Ga, circles — ^{71}Ga. Filled and empty symbols — β-Ga and α-Ga respectively. Solid lines — fitting curves.
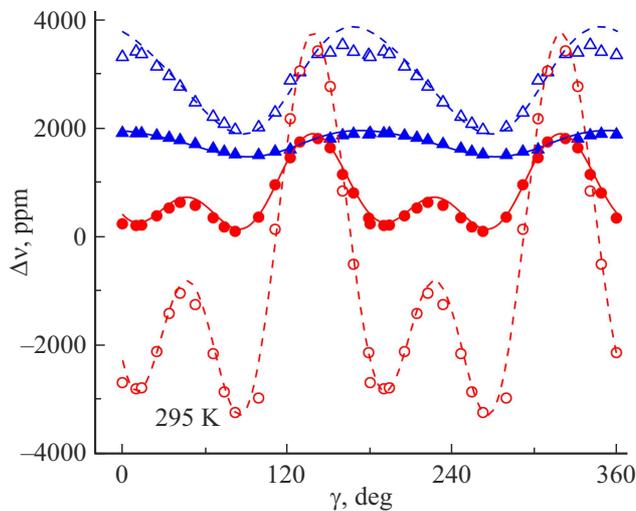
Figure 6. NMR lines shifts in the oriented α-Ga versus the angle of rotation γ for ^{69}Ga and ^{71}Ga (empty and filled symbols respectively) for the two magnetically nonequivalent sites. Solid and dashed lines — fits using formulae (2)−(4).

results obtained are consistent with the data presented in [11] for another sample of bulk gallium.

Measurements similar to those described above were also carried out on DPX 300 and Avance 500 spectrometers in fields of 7 and 11.7 T, respectively. The temperature conditions of the measurements completely coincided. The temperatures of the phase transitions, the type of NMR

spectra, and positions of the resonance lines coincided with the results obtained for experiments using Avance 400 spectrometer in 9.4 T field. However, the relative intensity of NMR lines associated with the oriented α-Ga and β-Ga, was higher in the case of 11.7 T magnetic field. The estimates showed that the proportion of oriented phases formed in 11.7 T field was 0.4, while the proportion of oriented phases formed in 7 T field was less than in 9.4 T field and was 0.24. This result suggests that the orienting effect of the magnetic field on gallium crystallization increases in stronger fields.

Figure 5 shows the curves of the NMR line recovery after inversion for ^{69}Ga and ^{71}Ga isotopes at a temperature of 295 K, for the line with a 220 ppm shift in the oriented α-phase and at a temperature of 260 K for the oriented β-phase. The measurements were carried out using Avance 400 spectrometer. Figure 5 shows that NMR line recovery is described by an exponential law. The time of spin-lattice relaxation for the oriented α-Ga turned out to be $T_1^{69} = 1550 \pm 150\,\mu$s and $T_1^{71} = 1000 \pm 100\,\mu$s. It should be emphasized that for the 1940 ppm shift line, the relaxation times were the same within the margin of error. The times of the spin-lattice relaxation for the oriented β-Ga were equal $T_1^{69} = 250 \pm 20\,\mu$s and $T_1^{71} = 160 \pm 20\,\mu$s.

To determine the direction of the crystalline axes in the oriented regions of α-Ga relative to the magnetic field, the frequency shifts of the resonance lines were observed depending on the angle of rotation of the sample around the horizontal axis perpendicular to the field direction and coinciding with the axis of the spectrometer coil. Measurements were carried out for both isotopes of gallium at 295 K. The rotation angle γ was calculated from the position of the sample after it was heated to 314 K and then cooled. The experimental results for two resonance lines in ^{69}Ga and ^{71}Ga spectra are shown in Figure 6.

4. Discussion

The appearance of narrow NMR lines during gallium freezing clearly indicates the formation of oriented regions of both α-Ga and β-Ga, which is in complete agreement with the results presented in [11]. Earlier, when observing orientational crystallization in the magnetic fields [2], it was assumed that the minimum magnetic energy of the nuclei of the crystalline phase formed during cooling of the melt corresponds to the energetically favorable directions of the crystalline axes. The angular dependence of the magnetic energy is due to the anisotropy of the magnetic susceptibility tensor. Thus, a strong magnetic field, in general, can influence the orientation of nuclei in any materials with an anisotropic crystal structure [3]. Given the small diamagnetic susceptibility of solid gallium, its magnetic energy density

can be written as:

$$U_m = -\frac{\chi}{2} B^2, \qquad (1)$$

where χ is the susceptibility corresponding to the specific orientation of the nucleus in the field. The susceptibility of α-Ga along the crystallographic axes a, b and c defined experimentally make [22]: $\chi_a = -8.82 \cdot 10^{-6}$, $\chi_b = -30.86 \cdot 10^{-6}$, $\chi_c = -16.99 \cdot 10^{-6}$. The codirection of the crystalline a axis and the magnetic field corresponds to the minimum of magnetic energy. Thus, a axis in the oriented α-Ga is expected to be oriented vertically parallel to the spectrometers' magnetic field. However, the orientation of a axis along the field may be incomplete due to the viscosity of the melt, which makes it difficult for the crystal nuclei to rotate [5]. Deviations in the orientation of a axis lead to small shifts of the resonance lines in repeated heating-cooling cycles, which is consistent with some difference in the positions of the lines in Figure 3, a and 3, c.

To confirm the dominant role of magnetic anisotropy in the orientational crystallization of α-Ga, we analyzed in detail the angular dependence of the NMR spectra shown in Figure 6.

Space group of α-Ga is Cmce (number 64). The unit cell contains 8 atoms divided into two groups with the same values of the quadrupole frequency ν_Q and the asymmetry η, but with different orientations of the principal axes of the electric field gradient (EFG) tensor relative to the crystalline axes [16]. The values ν_Q and η at temperatures down to 4.2 K were found in [16]. The components of the Knight shift tensor are given in [17]. From the findings of [16,17] it follows that the angular dependence of the position of resonance lines in α-Ga is determined mainly by the quadrupole interaction. However, the isotropic Knight shift in solid gallium significantly exceeds the quadrupole shifts and leads to higher resonance frequencies with the rise of temperature, whereas the quadrupole interaction declines with increasing temperature. In the gallium melt, the position of the NMR line is determined by the isotropic Knight shift, which decreases with increasing temperature [23,24]. The experimental data presented in Figure 2 are consistent with the results of [16,17,23,24].

The total shift of resonance line $\Delta \nu$ in α-Ga consists of an isotropic Knight shift K_{iso} and a quadrupole shift Q depending on the directions of the crystalline axes:

$$\Delta\nu = K_{iso} + Q. \qquad (2)$$

The quadrupole shifts of the lines corresponding to the central transitions $+1/2 \leftrightarrow -1/2$ in a strong field can be calculated using second-order perturbation theory [25]. The quadrupole shift Q for spin 3/2 is written as the sum of the isotropic and anisotropic parts:

$$Q = Q_{iso} + Q_{an} = -\frac{\nu_Q^2}{10\nu_L}\left(1 - \frac{\eta^2}{3}\right)$$
$$- \frac{\nu_Q^2}{2\nu_L}\left[A(\varphi,\eta)\cos\theta + B(\varphi,\eta)\cos^2\theta + C(\varphi,\eta)\right], \quad (3)$$

where ν_L is the Larmor frequency, θ and φ are the polar angles that determine the direction of the magnetic field relative to the principle axes of the EFG tensor. The coefficients in the second term are given by the expressions:

$$A(\varphi,\eta) = -\frac{27}{8} - \frac{9}{4}\eta\cos 2\varphi - \frac{3}{8}\eta^2\cos^2 2\varphi,$$

$$B(\varphi,\eta) = \frac{15}{4} - \frac{1}{2}\eta^2 + 2\eta\cos 2\varphi + \frac{3}{4}\eta^2\cos^2 2\varphi,$$

$$C(\varphi,\eta) = -\frac{23}{40} - \frac{14}{15}\eta^2 + \frac{1}{4}\eta\cos 2\varphi - \frac{3}{8}\eta^2\cos^2 2\varphi. \quad (4)$$

The isotropic Knight shift at room temperature is 1310 ppm [17]. The quadrupole frequency $\nu_Q = 10.88$ MHz for ^{69}Ga and the asymmetry of $\eta = 0.171$ are taken from [16], as well as data on the orientation of the principle axes of EFG tensor relative to the crystalline axes. The quadrupole frequency ^{71}Ga was calculated from the value for ^{69}Ga, since these frequencies differ by a multiplier equal to the square of the ratio of quadrupole moments [26]. The theoretical curves in Figure 6 were calculated based on the relations $(2)-(4)$ assuming that the axis a in the oriented α-Ga was initially directed along the magnetic field of the spectrometer. In this case, the rotation angle γ is equal to the angle between the magnetic field and a axis. Thus, studies of the angular dependence of the positions of the resonance lines confirm the dominant role of magnetic anisotropy in the orientational crystallization of gallium.

Metastable β-Ga has a monoclinic symmetry (space group C2/c). The signal of ^{71}Ga from polycrystalline β-Ga observed in [27] corresponded to the central transition and was strongly quadrupole-broadened. The half-width of the resonance line was 400 times greater than the half-width of the line from the oriented β-Ga (insert in Figure 4). A single line from the oriented β-Ga (unlike the two lines for α-Ga) indicates that all gallium atoms are magnetically equivalent.

Nuclear spin-lattice relaxation of quadrupole nuclei in conductors occurs mainly due to the interaction of nuclear magnetic moments with conduction electrons and due to the interaction of nuclear quadrupole moments with dynamic gradients of electric fields caused by the movement of atoms [28]. For nuclei in a rigid lattice, the second relaxation mechanism is ineffective. In case of purely dipole relaxation, the ratio of the spin-lattice relaxation times for two gallium isotopes should satisfy the equality: $T_1^{69}/T_1^{71} = \gamma_{71}^2/\gamma_{69}^2 = 1.61$. The relaxation times we obtained for α-Ga and β-Ga (Figure 5) agree with this ratio within the experimental accuracy, which confirms the dominance of the dipole relaxation mechanism in oriented gallium phases, similarly to the crystalline gallium powder according to nuclear quadrupole resonance data [29].

Conclusion

The NMR method has unambiguously demonstrated the formation of oriented regions of stable α-Ga and metastable β-Ga during crystallization of a gallium melt in a strong

magnetic field. Directional solidification was observed when narrow resonance lines corresponding to central transitions $+1/2 \leftrightarrow -1/2$ and typical for single-crystalline samples appeared in the NMR spectra of both gallium isotopes. Based on the intensity of the lines, it was found that the oriented regions accounted for about 1/4 of the total amount of the crystalline phase in the field 7 T and 1/3 in the field 9.4 T. The proportion of oriented regions increased to 0.4 in the field 11.7 T, which indicates the growth of orienting influence with increasing magnetic field. For α-Ga, it is shown that the crystalline axis a in the oriented regions was directed along the magnetic field. This confirms the well-known assumption about the dominant role of the magnetic energy of the nuclei of the crystalline phase in the phenomenon of directional crystallization. The results of measurements of the spin-lattice relaxation times of gallium isotopes in oriented α-Ga are consistent with the dipole relaxation mechanism due to interaction with conduction electrons.

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Conflict of interest

The authors declare that they have no conflict of interest.

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