Temperature effects in quadrupole interaction in NbHf alloys

V. A. Klyucharev, V. P. Bozhko, and A. S. Bulatov
Physico-technical Institute, Ukrainian Academy of Sciences
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Quadrupole interaction in NbHf alloys containing 0.035, 0.1, 0.25, 0.5, 2, 10, 20 and 50 at.% of Hf is studied in the normal (T = 300, 78 and 20°K) and superconducting phases (4.2°K) by the perturbed angular $\gamma\gamma$-correlation technique. A change in the smearing out of the local electric field gradient in alloys containing 2 and 10 at.% Hf is observed in the normal phase on lowering of the temperature from 300 to 78°K. No changes in the quadrupole coupling parameters are observed in the 300—20°K temperature range. Qualitative changes in the nature of quadrupole coupling are observed in the superconducting phases of alloys containing 2, 10 and 50 at.% of Hf but at present cannot be interpreted.

In the present study we used the method of perturbed angular $\gamma\gamma$ correlations (PAC) to search for and investigate temperature effects in quadrupole interaction in a disordered solid solution of hafnium and niobium, which crystallizes in a body-centered cubic structure. We had previously thoroughly investigated[1-3] the dependence of the parameters of the quadrupole coupling in the NbHf system on the Hf content. The obtained experimental data give grounds for hoping that the change of the electronic state which occurs when NbHf alloys become superconducting can lead to measurable effects for which a second-order phase transition may be responsible.

There have been some unsuccessful attempts to observe in practice the influence of the superconducting transition on the quadrupole interaction with the aid of γ resonance in crystals (see, for example,[4]). As shown by one of us[5], the PAC system makes it possible to measure the parameters of the quadrupole coupling more accurately than in γ-resonance experiments, and in addition, in the differential variant the PAC method yields more information, since it makes it possible to measure not only the frequency ω_0 of the quadrupole precession, the parameter δ of the smearing of the electric field gradient (EFG), and the asymmetry parameter η, but also to assess the spatial distribution of the EFG in a polycrystalline sample and the temporal characteristics of the interaction that leads to perturbation of the angular corelation function of the nuclear $\gamma\gamma$ cascade[6].

In the present investigation, the transmitting nucleus was ^{181}Ta, which is formed in β decay of ^{181}Hf, which is obtained when the nucleus ^{180}Hf captures a neutron. The previously observed relation between the frequency of the quadrupole precession in disordered metallic substitutional solid solutions with cubic crystal structure[2] served as the basis for the preparation of samples that ensured variation of ω_0 from 10 to 800 MHz, and made it possible by the same token to realize the optimal conditions for the study of all the aspects of the quadrupole interaction in the NbHf system in the normal and superconducting phases.

NbHf alloys containing 0.035, 0.1, 0.25, 0.5, 2, 10, 20, and 50 at.% Hf were prepared by the method of argon-arc melting. After activation in a reactor, they were homogenized in a vacuum of 10^{-6} Torr at a temperature of 1000°C for 10 hours. The investigated sample was placed in a glass cryostat, in which the boiling temperatures of liquid nitrogen, hydrogen, and helium were maintained at 760 mm Hg. Measurements of the delay-time dependence A(t) of the anisotropy of the angular corelation function of the $\gamma\gamma$ cascade 130—482 kV were carried out in all cases under conditions of constant geometry, so as to preclude the need for introducing corrections. The measurement procedure, the reduction of the experimental data, and the measurement setup have been described earlier[7].

TEMPERATURE EFFECTS IN THE NORMAL PHASE

The quadrupole interaction in the normal phase was investigated at temperatures 300, 78, and 20°K. In most of the alloys investigated there were no noticeable temperature effects. The quadrupole interactions correspond to the static quadrupole coupling in polycrystalline sources with parameters $\delta = 0.35$, $\eta = 0$, $\omega_0 = 290(1 - e^{-11c})$ MHz, where c is the hafnium content in the alloy in absolute units.

In alloys containing 10, 2, and sometimes 0.5 at.% Hf, we have observed differences in the A(t) dependences measured at 300 and 78°K, whereas the data for 78 and 20° agree within the limits of the statistical errors. The corresponding experimental results are given in Fig. 1. Table I gives the parameters of the quadrupole coupling for these alloys. This effect can also take place in alloys containing less than 2% HF but in the obtained range of delay times (50—60 nsec), it is impossible to observe it.

The results obtained in earlier investigations[1,2], and also in the present paper, offer convincing evidence that the quantity $\delta = 0.35$ characterizes the degree of disorder of the distribution of the impurity in a substitutional solid solution, so that it is difficult to assume that an increase of the temperature in the system in a region quite remote from the melting temperature can lead to some change in the distribution of the Hf impurities in the Nb. Since it is impossible to present a static mechanism capable of accounting for the temperature variation of δ, we must consider the possibilities connected with the thermal vibrations of the atoms. A nucleus executing thermal vibrations relative to a lattice site interacts with an alternating EFG, the magnitude of which is connected with the amplitude of the oscillations. Since the period of thermal vibrations is much smaller than the averaging time in the PAC method ($\approx 10^{-9}$ sec), this leads to an additional smearing of the EFG.

Since the thermal oscillations are not completely frozen out, the absence of a temperature dependence of

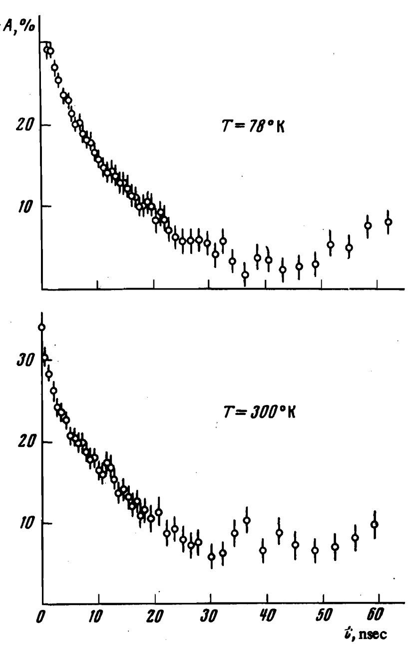

FIG. 1. A(t) for NbHf alloy containing 2 at. % Hf.

TABLE 1

c, at.%	T = 300° K		T = 78°, 20° K	
	ω_0, MHz	δ	ω_0, MHz	δ
10	200 ± 10	0.5±0.05	200 ± 10	0.35 ± 0,05
2	75 ± 10	1	75 ± 10	0.35 ± 0,05

δ in the temperature range 78–20°K on the one hand, and at large Hf concentrations on the other, leads to the following conclusions. The amplitude of the thermal oscillations of the atoms is, as a rule, too small for the deviations of the ions from the centers of the cubic symmetry to give a measurable effect in the quadrupole interaction. At the same time, as the Hf content is decreased the amplitude of the thermal vibrations of the impurity atoms at T = 300°K can reach anomalously large values, whereas at 78°K this effect is not observed, at least for alloys containing 1 at.% Hf and more. It follows therefore that at high temperatures the impurity atoms have a larger free energy, and this can be the cause of formation of clusters of impurity Hf and Ta atoms in Nb, a phenomenon observed earlier[2].

QUADRUPOLE INTERACTION IN THE SUPERCONDUCTING PHASE

Since it was established experimentally that at 78 and 20°K there are no temperature effects whatever in the quadrupole interaction in any of the investigated alloys, it could be assumed that we would be able to observe even weak changes in the magnitude or character of the quadrupole coupling when the NbHf alloys became superconducting. Unfortunately, we were unable to vary the temperature at $T < T_c$, so that all the measurements were performed at 4.2°K. In alloys with 0.1, 0.25, and 0.5 at.% Hf, within the limits of measurement errors, we did not observe any convincing difference in the quadrupole interaction in the normal phase (at 78 and 20°K) and in the superconducting phase. In the sample with 0.035 at.% Hf, at the same temperatures, there was certainly no such difference. Finally, in alloys with 2, 10, and 50 at.% Hf there are differences

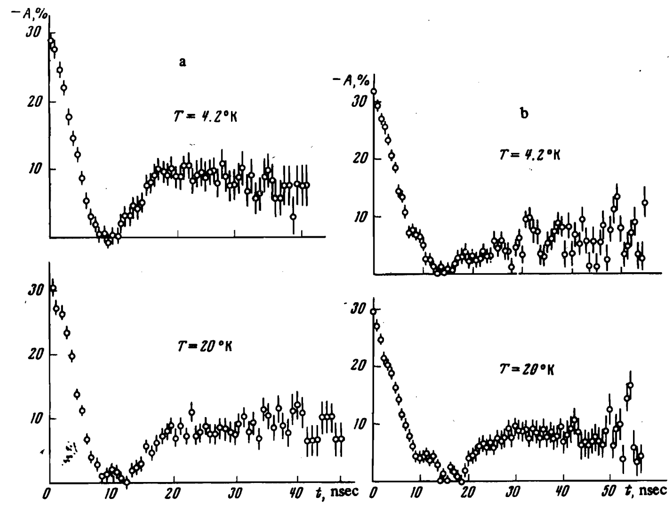

FIG. 2. A(t) for NbHf alloys containing 50 (a) and 10 (b) at. % Hf.

in the A(t) dependences that cannot be due to methodological factors (see Fig. 2).

The differences in the character of the perturbation of the angular correlation in the normal and superconducting phases reduces in general to the following. First, the fitting of the experimental A(t) dependence for the static quadrupole interaction in a polycrystalline source, which makes it possible to obtain the parameters of the quadrupole coupling for the normal phase with sufficient accuracy, gives a much worse approximation for the superconducting phase, and no variation of the parameters improves it. This fact indicates a change in the character of the quadrupole coupling. Second, alloys with 10 and 50 at.% Hf are characterized by a decrease in the anisotropy (in comparison with the normal phase) with increasing delay times at t > 20 nsec, and for the latter alloy the decrease of the anisotropy is observed even in the region of the so-called "hard core" of the angular correlation. Third, as seen from Table II, there is a systematic difference in the frequencies of the quadrupole precession in both phases. It should be noted immediately that this difference can be the result of the aforementioned difference in the character of the quadrupole coupling in the normal and superconducting phases.

We see that the experimental manifestation of the difference in the quadrupole coupling is not distinct enough for its reliable interpretation, but the systematic blockage of the anisotropy of the angular correlation function at larger delays, and the ensuing poor approximation of the analytic A(t) dependence for the static quadrupole coupling to the experimental results, give grounds for assuming that in the superconducting phase there appears, besides the usual static quadrupole interaction, an additional time-dependent coupling that is similar to that typical of liquids[6].

TABLE 2

c, %	T = 20° K		T = 4° K	
	ω_0, MHz	δ	ω_0, MHz	δ
50	280 ± 6	0.35 ± 0.05	305 ± 10	0.35 ± 0.10
10	200 ± 6	0.35 ± 0.05	220 ± 10	0.35 ± 0.10
2	75 ± 5	0.35 ± 0.05	80 ± 10	0.35 ± 0.10

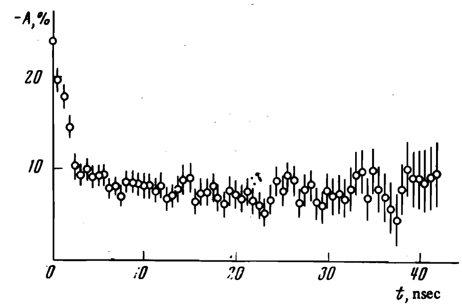

FIG. 3. A(t) for NbHf alloy containing 0.035% Hf, T = 4.2°K.

It is interesting to note that the interaction of the fluctuating EFG with the nuclear quadrupole moment is equivalent under definite conditions to a radiative broadening of a nuclear level[8]. Therefore the assumption that the nonstatic quadrupole interaction makes a contribution to the superconducting phase agrees with the results of measurement of the nuclear magnetic resonance in vanadium alloys of the type V_3X[9]. It was observed in[9] that the NMR line broadens appreciably as the temperature drops near T_c.

Of definite interest are the results of measurements of the PAC in an alloy containing 0.035 at.% Hf (see Fig. 3). In this case, all the Hf atoms are connected in clusters of impurity atoms, and as a result of the large local concentration of impurity atoms (and consequently of the large value of ω_0), the anisotropy of the angular correlation function drops after 3–4 nsec to the "hard core" value—the minimum anisotropy in the polycrystalline material with arbitrarily strong quadrupole coupling. It is easily seen that no blockage of the anisotropy takes place with increasing delay time in this case, and the A(t) dependences are the same for both phases. If the changes in the character of the PAC that are observed in superconducting alloys are indeed connected with a second-order phase transition, then the result for an alloy with 0.035 at.% Hf indicate that the clusters of impurity atoms do not go over into the superconducting state at all. On the other hand, since the formation of impurity clusters leads to an effective purification of the niobium matrix, this fact can be connected with the increased value of T_c in niobium doped with hafnium[10].

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149