

CONCENTRATION DEPENDENCE OF THE ELECTRIC FIELD GRADIENT IN THE NbHf SYSTEM

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The dependence of the quadrupole precession frequency ω_0 in NbHf alloys on the hafnium concentration was measured by the method of perturbed angular correlations. In the investigated range of concentrations (0.035–50 at. %) the alloys crystallize into a body-centered cubic lattice. The parameters of the quadrupole interaction were obtained from the differential angular correlation function of the $\gamma\gamma$ cascade 133–482 keV in ^{181}Ta . The variation of ω_0 with the hafnium concentration (c) is well described by the empirical relation $\omega_0 = 290 [1 - \exp(-11c)]$ MHz. The frequency smearing is $\delta = \Delta\omega_0/\omega_0 = 0.35$ for all the investigated samples. In alloys with 10% of Hf and less, there is observed a contribution of the quadrupole interaction with frequency ω'_0 , which increases with decreasing hafnium content. The anomalous behavior of ω'_0 may be connected with the violation of the statistical distribution of the impurities in the niobium and with formation of associations of impurity atoms.

IN spite of the fact that there are many investigations of the electric quadrupole interaction in matter, there is still no sufficiently well founded model within the framework for which it is possible to calculate reliably the electric field gradient (EFG) at the nucleus. Consequently it is impossible as a rule to determine from the experimental data on the quadrupole-interaction constant the nuclear quadrupole moment Q , the EFG in the lattice V_{ZZ} , and the antiscreening factor γ_∞ . At the same time, direct experimental information concerning each of these quantities is of considerable interest. It suffices to know that Q is the only nuclear parameter which is not measured by a direct method.

It is assumed that the EFG can be calculated in the simplest manner for a cubic crystal lattice with impurities. In this case, owing to the high symmetry of the matrix, the EFG in the region of the nucleus is due principally to the effective impurity charges, if the symmetry of their distribution in the lattice is lower than cubic. Measurement of the quadrupole precession frequency ω_0 in a disordered cubic solid solution makes it possible to obtain the dependence of the EFG at the nucleus on the average distance between impurity atoms.

The classical method of measuring ω_0 —nuclear quadrupole resonance—is insufficiently effective in research of this type, owing to the need for measuring ω_0 in a wide range of frequencies. Additional difficulties are due to the skin effect and to the smearing of the frequency of quadrupole interaction^[1]. The latter circumstance decreases the effectiveness of the known non-resonant method of investigating the quadrupole interaction, based on the Mössbauer effect.

The EFG in disordered solid solutions can be effectively investigated with the aid of perturbed angular correlations (PAC) of nuclear radiations^[2], since this method permits a measurement of the quadrupole-interaction frequency in a wide range (1–10³ MHz) and with sufficiently high accuracy (1–10%). The smearing of the EFG at the nucleus can likewise be measured by the PAC method, and consequently the increase in the error of the measurement of ω_0 will be small.

The concentration dependence of the EFG in the lattice of silver with impurities was investigated in^[3] by the PAC method, but in view of the use of the integral variant of the method, the authors could investigate only systems with impurity concentrations 0.25–1.0%.

The differential PAC method^[4] makes it possible to obtain reliable information concerning all the parameters of the quadrupole interaction (ω_0 , the EFG non-axiality parameter η , and the EFG smearing parameter δ), and is a convenient tool for the investigation of the nuclear quadrupole interaction. We have used this variant of the PAC method to study the EFG produced by impurity hafnium atoms in the body-centered cubic lattice of niobium. NbHf alloys containing 0.035, 0.1, 0.25, 0.5, 2, 10, 20, and 50 at. % of hafnium were prepared by arc melting in an argon atmosphere. The samples were homogenized for 8 hr at 1000°C in a vacuum of 10⁻⁶ Torr.

X-ray structure investigations have shown that all the alloys were single-phase and had a BCC structure. The samples were activated in the reactor of the L. Ya. Karpov Physico-chemical Institute.

We measured the differential angular correlation function of the $\gamma\gamma$ cascade 133–482 keV of ^{181}Ta , which is produced as the result of the β decay of ^{181}Hf . The procedure for the PAC measurements and the measuring apparatus are described in^[4,5]. For each NbHf alloy we registered $(2-3) \times 10^6$ coincidences.

Information on the parameters of the quadrupole interaction was extracted from the measured temporal dependence of the anisotropy of the angular correlation function by fitting the theoretical expression for the anisotropy by varying the parameters ω_0 and δ . Fitting with allowance for the final resolving time of the measuring system was with the aid of a computer.

The measured and calculated values of the anisotropy as functions of the γ_{482} delay time are shown in Fig. 1 and 2. The EFG smearing parameter for all alloys with $c_{\text{Hf}} \geq 2\%$ is practically the same and equals $\delta = 0.35 \pm 0.05$; the dependence of ω_0 on the hafnium concentration is shown in Fig. 3. The variation of ω_0 with the Hf

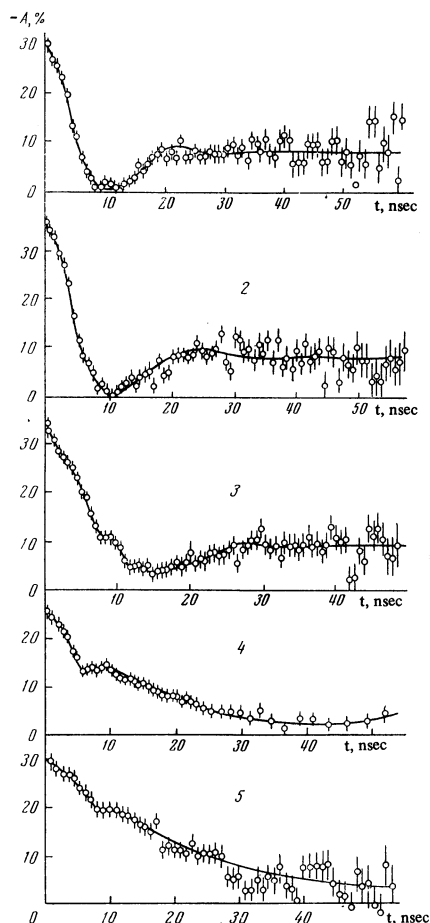


FIG. 1. Time dependence of the anisotropy $A(t)$ for NbHf alloys with the following Hf content: 1—50, 2—20, 3—10, 4—2, 5—0.5%. The solid curves were calculated with parameters ω_0 , $\delta = 0.35 \pm 0.05$, and $\eta = 0$.

concentration is given by the empirical relation

$$\omega_0 = 290[1 - \exp(-11c)] \text{ MHz}, \quad (1)$$

which is shown by the solid line.

Since the NbHf system is a typical disordered substitution solution with cubic crystal structure, one can expect the quadrupole-interaction frequency to be described in systems of this type by the expression

$$\omega_0 = \omega_0^0 [1 - \exp(-\alpha c)], \quad (2)$$

where ω_0^0 and α are empirical parameters, the meaning of which can be clarified in subsequent investigations. Expression (2) can be rewritten in the form

$$V_{zz} = V_{zz}^0 [1 - \exp(-\alpha c)], \quad (3)$$

since ω_0 is proportional to the field gradient V_{ZZ} produced by the charges in the lattice at the location of the nucleus. There is no doubt that the empirical parameters V_{ZZ}^0 and α are connected with the averaged characteristics of the NbHf by means of the lattice parameter a and by the effective charge of the impurity Z_{eff} , but the data obtained in the present investigation are insufficient to disclose this connection.

At Hf concentrations of 10% and less, the $A(t)$ dependence has a complicated character and corresponds to a

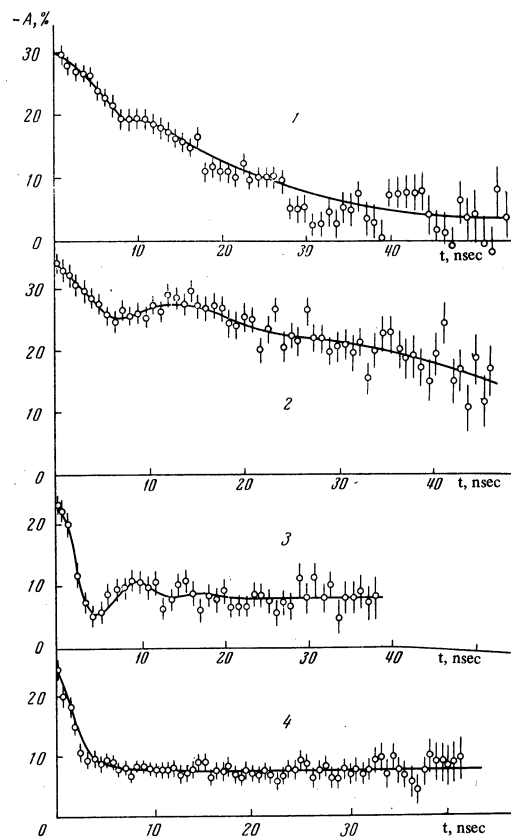


FIG. 2. Time dependence of the anisotropy $A(t)$ of alloys with Hf contents: 1—0.5, 2—0.25, 3—0.1, 4—0.035%.

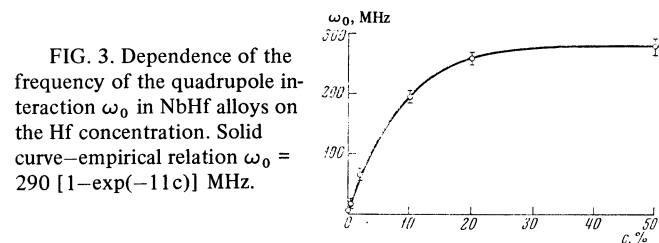


FIG. 3. Dependence of the frequency of the quadrupole interaction ω_0 in NbHf alloys on the Hf concentration. Solid curve—empirical relation $\omega_0 = 290 [1 - \exp(-11c)]$ MHz.

superposition of quadrupole interaction with two different frequencies ω_0 and ω'_0 , the contribution of the frequency ω_0 in the alloys containing 0.035 and 0.1% of Hf being immeasurably small (see Figs. 1 and 2). The solid lines in Fig. 2 show the calculated curves $A(t) = \beta A(\omega_0, t) + (1 - \beta)A(\omega'_0, t)$, where β is the statistical weight of the quadrupole interaction with frequency ω_0 . The dependence of ω_0 and ω'_0 on the Hf concentration is shown in Fig. 4, where the solid line shows the empirical relation $\omega'_0 = 620 \exp(-1.35c)$ MHz and the dashed line shows the dependence $\omega_0 = (4000c)$ MHz (c is in absolute units).

The presence of two quadrupole-interaction frequencies cannot be explained within the framework of the representation of the disordered solid solution as a niobium matrix with randomly distributed impurities. If the hafnium atoms constitute the only small impurity in the niobium, then $\omega_0 \approx \text{const} \cdot c^{[3]}$, i.e., the EFG is described sufficiently well by the expression $V_{ZZ} \approx 2Z_{\text{eff}}/r^3$, where r is the average distance between

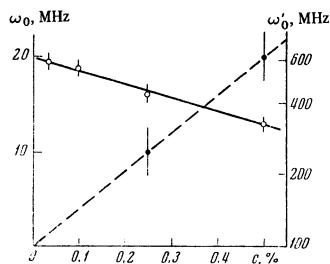


FIG. 4. Dependence of ω_0 and ω'_0 on the Hf concentration, ●—experimental values of ω_0 ; ○—experimental values of ω'_0 ; solid line—empirical $\omega'_0(c)$ dependence, dashed— $\omega_0(c)$.

impurity atoms and is connected with the average distance \bar{a} between the atoms in the lattice by the relation $c = \bar{a}^3/r^3$ (c is the impurity concentration and \bar{a} is determined by the packing density and by the lattice parameter a).

It is obvious that at small c_{Hf} the system NbHf cannot be regarded as a binary one, since the niobium contains extraneous impurities. In view of the additivity of the charge, the extraneous impurities X should give a constant contribution (since $c_{\text{X}} = \text{const}$) to the quadrupole interaction and we can expect for ω_0 a relation $\omega_0 = \omega_{0\text{X}} + \text{const } c_{\text{Hf}}$ (at $c_{\text{Hf}} \sim c_{\text{X}} \ll 1$).

A presence of two quadrupole-interaction frequencies is evidence of qualitatively different surroundings of the transmitting nuclei in the Nb + Hf + X system. The frequency ω_0 corresponds to the surrounding in the system Nb + Hf, and ω'_0 to the system Hf + X. The value of ω'_0 at $c_{\text{Hf}} \leq c_{\text{X}}$ exceeds the value of ω_0 at $c_{\text{Hf}} = 50\%$, which it follows that the average distance between the Hf and the impurity X atoms is close to a , for otherwise we would have to assign to the impurity X an unreason-

ably large value of Z_{eff} ($c_{\text{X}} = 0.1\%$ corresponds to $r \approx 10a$).

It follows therefore that associations of the atoms Hf + X are produced in the Nb + Hf + X system before the crystallization. Since ω'_0 depends on the ratio of c_{Hf} and c_{X} , it is doubtful that the associations are chemical compounds. The probability of formation of associations is quite large, for even at $c_{\text{Hf}} \approx c_{\text{X}}$ (alloy with $c_{\text{Hf}} = 0.1\%$) the contribution of ω_0 amounts to less than 5%.

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