Point defects produced in LiF by (n,γ) reactions with thermal neutrons

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The method of radioactive registration of NMR was used to determine the type of point defects produced in an LiF crystal by γ recoil of the radioactive nuclei ^{8}Li ($T_{1/2}=0.84$ sec). The constant of the quadrupole interaction of the ^{8}Li nuclei with the defects, the activation enthalpy, and the lifetime of the defects were measured in the temperature range 13–295 K.

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Polarized β-active recoil nuclei produced in nuclear reactions serve as convenient probes for the study of the crystal-lattice defects that they produce. By observing the angular anisotropy of the β radiation of these nuclei we can study their spin evolution perturbed by the interaction with the surrounding defects.

We have investigated point defects in LiF crystals by the method of nuclear magnetic resonant (NMR) with the β-active recoil nuclei ^{8}Li produced in the reaction ^{7}Li(n,γ) ^{8}Li with thermal polarized neutrons. After emission of the captured γ quanta, the energy of the recoil nucleus is ~ 300 eV, so that the production of several vacancy-interstice pairs per ^{8}Li nucleus can be expected. By locally perturbing the cubic symmetry of the crystal, the point defects produce an electric field gradient at the ^{8}Li nucleus. In the case of a defect close to the nucleus, splitting of the NMR line should take place, but if the defects are remote, broadening of the line can be expected. Earlier measurements[1] made on LiF samples at room temperature did not reveal a noticeable influence of defects of the NMR line shape of the β-active ^{8}Li nuclei, thus attesting to the annealing of the latter at this temperature. Lowering the sample temperature, however, can lead to a "freezing" of the defects and to the appearance of a quadrupole structure in the NMR spectrum.

Resonant polarization of the β-active nuclei in the presence of an external radio-frequency (RF) field and a magnetic field was theoretically described by solutions of the equations of motion for the spin density matrix with a Hamiltonian containing a term corresponding to quadrupole interaction with a single defect. The parameters of the theory were the probability w of defect formation, the lifetime μ^{-1} of the defect, and the quadrupole-interaction constant $\beta/\gamma=\omega_Q/2\gamma(\omega_Q$ is the frequency of the quadrupole interaction[7] and γ is the gyromagnetic ratio for the ^{8}Li nucleus).

The β-radiation asymmetry ϵ, which is proportional to the polarization, was calculated from the formula $\epsilon=[N_i(0)-N_i(\pi)]/[N_i(0)+N_i(\pi)]$, where $N_i(0)$ and $N_i(\pi)$ are the numbers of decay electrons registered by two scintillation β counters ($i=1,2$) placed at angles 0 and π to the direction of the polarization of the ^{8}Li nuclei. For more details on the apparatus see[3].

The measurements were made on two single-crystal samples with crystallographic axes [111] and [100] oriented parallel to the external magnetic field. Figure 1

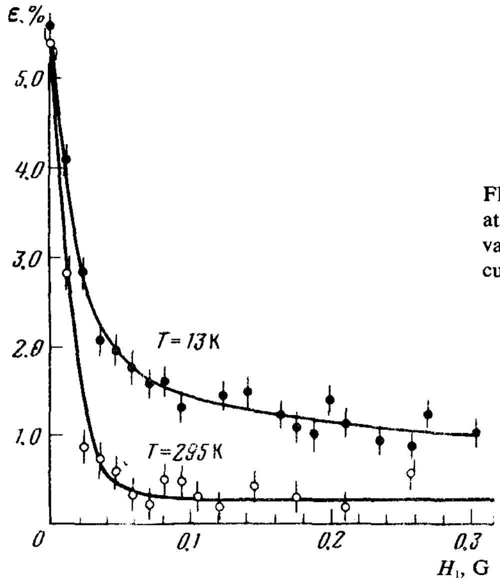

FIG. 1. Dependence of the anisotropy of the β radiation on the amplitude of the RF field at the resonant value of the frequency $\nu_0(^8Li)=2404.5$ kHz. Solid curves–theoretical calculation.

shows data on the resonant depolarization of the ^{8}Li nuclei as a function of the amplitude of the RF field, for the [111] sample, at two temperatures. It is seen that at room temperature it is possible to obtain complete depolarization of the ^{8}Li nuclei at an RF

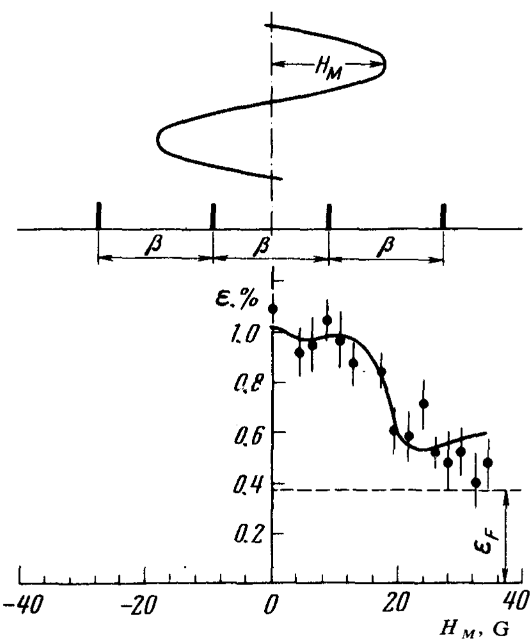

FIG. 2. Dependence of the anisotropy of the β radiation on the modulation amplitude H_M of the external magnetic field. The parameters of the employed RF field at $H_1=0.21$ G and $\nu_0(^8Li)=2404.5$ kHz; ϵ_F is the anisotrpy of the β radiation of ^{20}F.

field amplitude $H_1 \gtrsim 0.1$ G. The residual asymmetry (at $H_1 \gtrsim 0.1$ G) is due to the background asymmetry of the β decay of ^{20}F. At these amplitudes, however, the ^8Li nuclei are not completely depolarized at low temperature. This can be attributed to the fact that some of the ^8Li nuclei have in their nearest environment point defects that shift the value of their resonant frequency on account of the quadrupole interaction. In fact, the use of an external magnetic field modulated with an amplitude comparable in magnitude with the quadrupole-interaction constant makes it possible to depolarize the ^8Li nuclei completely even at low temperatures. Figure 2 shows the obtained dependence of the resonant depolarization on the modulation amplitude H_M of the external magnetic field: $H = H_0 + H_M \sin 2\pi \nu_M t$ ($\nu_M = 50$ Hz). The solid line is the result of the reduction of the experimental data by least squares with allowance for the dipole-dipole width of the NMR line and for the inhomogeneity of the modulating field, at the following values of the parameters of the theory: $w = 0.18 \pm 0.02$, $\beta/\gamma = 18.1 \pm 0.7$ G. The position of the quadrupole-quartet lines obtained by this reduction (the spin of the ^8Li nucleus is $I = 2$) is shown schematically in the upper part of Fig. 2. The observed characteristic inflections on the curve correspond to the modulation amplitudes H_M at which the depolarization resonance conditions are satisfied for a new pair of lines of the quadrupole quartet.

As noted above, the theory presupposes the presence of only one defect near the β-active ^8Li nucleus. Actually, the probability of formation of two or more defects of the same type should be greatly decreased by their mutual Coulomb repulsion. The only possible defects are vacancies of fluorine and lithium and their interstices. The quadrupole interaction with the nearest vacancy of fluorine, when the [111] axis of the sample is parallel to H, is equal to zero (because of the corresponding direction cosine). The nearest lithium neighbors of the ^8Li nucleus occupy 12 positions, and the absolute value of the quadrupole interaction of a lithium vacancy in any position with the ^8Li nucleus is the same. A theoretical estimate of this interaction, neglecting the polarization of the medium, yields $\beta/\gamma = 14$ G, and if the medium is regarded as continuous we get $\beta/\gamma = 6.6$ G. The formation of the interstice leads to a constant $\beta/\gamma \sim 200$ G. We see that the experimentally obtained value of β/γ is closest to the value of the constant for a lithium vacancy in the case when the polarization of the medium is neglected.

To study the quadrupole interactions of the ^8Li nuclei with fluorine vacancies, NMR measurements were made on the crystal oriented with the [100] axis parallel to H. For this case, however, no noticeable influence of the quadrupole interactions on the line shape was observed, although previously[4] these vacancies (with the constant $\beta/\gamma = 74 \pm 10$ G) were detected under analogous conditions by their rapid depolarization of ^8Li nuclei. The fact that they exert no influence in the present experiment indicates that the lifetime of the fluorine vacancy is $\mu^{-1} \ll T_{1/2}$ even at 13 K.

Measurements of the resonant depolarization on the [111] sample at different temperatures have yielded the temperature dependence of the lifetime of the lithium vacancy. It is shown in Fig. 3, in the form of a plot of $\ln\mu$ against $1/T$. It is seen that this plot satisfies the Arrhenius law $\mu = \mu_0 \exp(-h_a/kT)$ with the parameter $\mu_0 = 10^{1.4 \pm 0.4}$ Hz and activation enthalpy $h_a = 0.030 \pm 0.006$ eV. The obtained en-

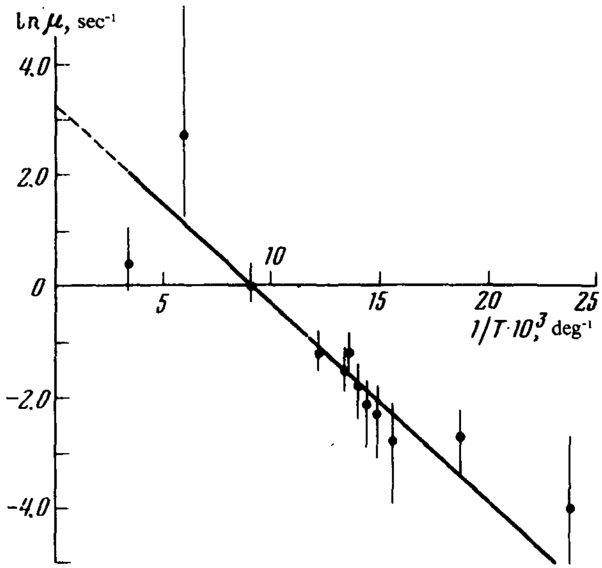

FIG. 3. Dependence of the lifetime of a lithium vacancy on the temperature. Straight line—Arrhenius law.

thalpy turned out to be much less than the values known in the literature and describing the migration of the vacancies ($h_a \sim 1$ eV[5]). It must therefore be concluded that the annealing of the lithium vacancies produced in γ recoil of ^{8}Li in LiF is the result of recombination of Frenkel pairs, and the obtained value of h_a describes the motion of the interstices. The value of the parameter μ_0 turned out to be much less than the Debye frequency ($\mu_0 \ll 10^{13}$ sec^{-1}). This may correspond qualitatively to a picture wherein the recombination of a crowdion with a vacancy takes place with a simultaneous "collective" displacement of all the ions situated between them.

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