NMR in $Nb_3Al_{1-x}Ge_x$ compounds

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The Knight shift k and spin-lattice relaxation time T_1 for ^{27}Al in $Nb_3Al_{1-x}Ge_x$ compounds were measured; it was found that for all these compounds having $x < 0.5$, $k = 0.012 \pm 0.003$ % at all temperatures from 20 to 200°K and $T_1 = 185$ msec at 78°K. The influence of cross effects on the longitudinal relaxation of aluminum is discussed. The NMR line shape for aluminum in $Nb_3Al_{0.75}Ge_{0.25}$ was examined at 20 °K and no additional splitting was detected; it is concluded that this compound probably does not undergo a low-temperature martensitic transformation. Whenever annealing raises the critical temperature of a specimen, the NMR spectrum is narrower after the heat treatment and the niobium echo envelope falls more sharply (T_2^* is shorter).

NMR, magnetic susceptibility, and electronic heat capacity measurements made in recent years have shown that the high critical superconducting temperatures T_C exhibited by compounds with the A-15 structure such as V_3X (X = Si, Ga, Ge) and Nb_3Sn are due to the high electron state density N(0) of resulting from the narrow-d-band structure. It was also found that the temperature dependence of the Knight shift $k \equiv \Delta H/H$ is stronger, the higher T_C.[1] On the other hand, the Knight shift in $Nb_3Al_{0.8}Ge_{0.2}$ is virtually temperature independent [2], although the critical temperature $T_C = 20.7°$ K of this compound is the highest known today [3]. The high critical temperatures of A-15 compounds are attributed to the quasi-one-dimensional motion of the electrons[4], it being assumed that T_C is higher, the more pronounced the one-dimensional character of the electron motion.

Here we report further results of our NMR studies of the $Nb_3Al_{1-x}Ge_x$ system. The NMR measurements make it possible to estimate the density of s and d states on the Fermi surface and to determine the extent to which the systems exhibit quasi-one-dimensional behavior.

EXPERIMENTAL TECHNIQUE

The specimens, each weighing 6 g, were prepared by fusing compacted niobium, aluminum, and germanium powders. The alloyed regulus was divided into two parts, one of which was annealed at 720° C for four days. The critical temperatures T_C for the bulk specimens were in good agreement with published values [3].

For NMR measurements it is desirable to use powders with grain diameters smaller than the skin depth for the rf field. The alloys are unusually brittle, so it was not difficult to reduce them to fine powders in an agate morter. In this way we obtained specimens with grain diameters of ~20 μm.[1] However, as the grinding proceeds the transition curve to the superconducting state broadens, the width of the transition region reaching in some cases 5–6°, although for a bulk specimen the transition region is only 0.2–0.3° wide [5]. Since the transition of the finely powdered materials began at a temperature that differed little from the critical temperature T_C for a bulk specimen, it was assumed that some of the grains have a high critical temperature. We used a magnetic method to separate these grains. The powders were cooled to 18° K and poured between the poles of an electromagnet. Since diamagnetic materials are ejected from a nonuniform magnetic field, the super-

conducting grains remained suspended while the "normal" grains fell through. Figure 1 shows transition curves for "normal" and separated powders.[2] It will be seen that the transition region is considerably narrower for the separated powder than for the unseparated one. In addition to the powders, we prepared two bulk specimens—thin plates 0.2 mm thick—of $Nb_3Al_{0.75}Ge_{0.25}$.

The Knight-shift measurements were made with a spectrometer having a superconducting solenoid. The equipment differed from that described in [6] only in that the superconducting solenoid produced a uniform field throughout a larger volume and correction of the field was effected with the aid of a slot on the inner winding. For measurements at higher temperatures the NMR pickup and the specimen were put into a metallic cryostat that could be filled with liquid hydrogen, neon, or nitrogen, depending on the temperature desired. The ^{27}Al NMR signals from the bulk specimens were very weak, so the signal from the synchronous detector was recorded on punched tape for subsequent processing on a "Nairi-2" computer. The data from 40–50 runs of 200 points each were subjected to the following very simple correlation analysis: The values y_i measured for the individual points were averaged with the two neighboring values, and then the new sequence $y_i^{(1)}$ was subjected to the same averaging procedure. This procedure sharply cut off the high-frequency noise and raised the signal-to-noise ratio to 30 or higher.

The relaxation measurements were made with a coherent crossed-coil spectrometer at a frequency of 12 MHz in the electromagnet, using a pulsed high-frequency field H_1 of 40 Oe. The over-all dead time of the receiver did not exceed 10 μsec. To improve the signal-to-noise ratio we used synchronous detection and a long-persistence oscillograph in the accumulation mode.
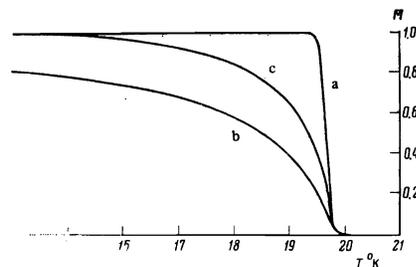
FIG. 1. Superconducting transition curves for $Nb_3Al_{0.8}Ge_{0.2}$ specimens: a—bulk specimen, b—fine powder, c—separated powder.

RESULTS AND DISCUSSION

A. The ^{27}Al Knight shift and spin-lattice relaxation

Our ^{27}Al NMR measurements on $Nb_3Al_{1-x}Ge_x$ specimens (with $x < 0.75$) showed that the Knight shift is small at 20.4° K and independent of the germanium concentration (at least with an accuracy of 0.003%). Figure 2 summarizes Knight-shift measurements on a large number of specimens, both powders and bulk specimens, including specimens of $Nb_3Al_{0.76}Ge_{0.25}$ with critical temperatures T_C ranging from 15 to 19.8° K. The absolute shift, corrected for the macroscopic paramagnetism, is $0.12 \pm 0.005\%$ at 20° K. The solenoid field was calibrated against the NMR of pure aluminum, the shift of which was taken as 0.162%. The error in determining the absolute shifts is somewhat larger in this case than when protons or nonmagnetic salt solutions are used.

On raising the temperature from 20 to 200° K the shift remains constant within $\pm 0.002\%$ for all the $Nb_3Al_{1-x}Ge_x$ specimens with $x < 0.5$ [2], while at room temperature the shift in Nb_3Al and $Nb_3Al_{0.75}Ge_{0.25}$ is about 0.007% greater. A similar increase in the shift for Nb_3Al was reported in [7]. In none of these cases, however, were the measurements accurate enough to permit one to say anything definite about the character of the temperature dependence.

There are two effects that might be responsible for the small ^{27}Al Knight shift: a low density of s states[8], or a large negative polarization contribution [9]. To separate these effects we determined the aluminum spin-lattice relaxation time T_1 from measurements of the recovery time of the induction drop or echo following ten 90° pulses. Figure 3 shows the measurements for several specimens at 78° K. These measurements gave $T_1T = 14.4 \pm 1.2$ sec-deg for the $Nb_3Al_{1-x}Ge_x$ specimens[3]
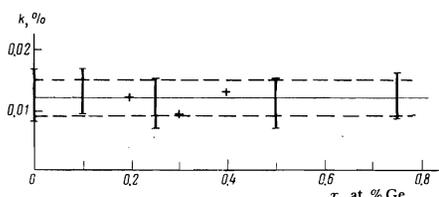
FIG. 2. The ^{27}Al Knight shift in $Nb_3 Al_{1-x} Ge_x$ compounds at 20.4°K.
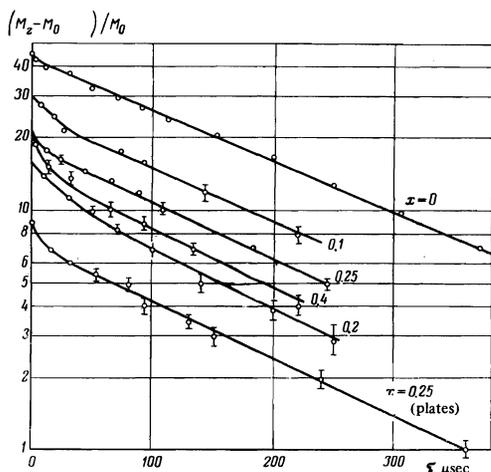
FIG. 3. Longitudinal magnetization drop vs. time at 78°K for $Nb_3 Al_{1-x} Ge_x$ specimens with $x < 0.4$.

with $x < 0.4$ and the considerably smaller value $T_1T = 9.2$ sec-deg for the specimen with $x = 0.75$.

Assuming that the ^{27}Al Knight shift k and relaxation time T_1 are entirely determined by the two effects mentioned above, we can write

$$k = k_s + k_{cp}, \quad k_{cp} < 0, \tag{1}$$

$$1/T_1 = 1/T_{1s} + 1/T_{1cp}, \tag{2}$$

where the subscripts s and cp indicate the contributions from the contact interaction and the polarization of the inner shells, respectively. Equations (1) and (2) are coupled by a relation of the Korringa type[9], so that the two contributions can be separated from the experimental values of k and T_1. Thus, we have

$$(T_1 T)^{-1} = \frac{4\pi k_B}{\hbar} \left(\frac{\gamma_{Al}}{\gamma_e}\right)^2 [k_s^2 + \varepsilon k_{cp}^2], \tag{3}$$

where k_B is Boltzmann's constant, γ_{Al} and γ_e are the gyromagnetic ratios for aluminum and the electron $(g = 2)$, respectively, and ε is a factor whose possible values [9] lie between 0.2 and 0.5. Solving (1) and (3) simultaneously, selecting the solution for which $k_{cp} < 0$, and taking account of the possible values of ε, we find

$$k_s \leqslant 5.05 \cdot 10^{-4}, \quad |k_{cp}| \leqslant 3.75 \cdot 10^{-4}.$$

These estimates are apparently too high. The polarization contribution as estimated from the concentration measurements of the Knight shift are lower by about a factor of 2. Actually, the polarization is stronger, the higher the d-state density at the Fermi level ($k_{cp} \sim N_d(0)$). Since $N_d \gg N_s$ [7], we can use data on the electronic heat capacity to determine how the polarization contribution should change when aluminum is replaced by germanium. The ratio of the electronic heat capacities of Nb_3Al and $Nb_3Al_{0.8}Ge_{0.2}$ is 72/59 [10], while the ^{27}Al Knight shift is constant within 0.003%. Assuming that this value determines the upper bound to the change in the polarization, we find $|k_{cp}| \leqslant 1.6 \cdot 10^{-4}$. Thus, for the contact contribution we obtain

$$0.012 \leqslant k_s \leqslant 0.028\%. \tag{4}$$

The spin-lattice relaxation time calculated with (3) for these values of the Knight shift are some 3.5 times longer than the experimental values. To interpret this discrepancy let us turn to the complete NMR spectrum of one of the $Nb_3Al_{0.8}Ge_{0.2}$ specimens shown in Fig. 5a. Since the aluminum and germanium lines overlap, cross relaxation[11] is possible. The aluminum nuclei interact by dipole coupling with the niobium nuclei, which soon transfer their excitation energy to the lattice. Let us suppose that the perturbation described by the correlation function $G(\tau) = \exp(-|\tau|/\tau_c)$ is due to the dipole interaction, and let us take the correlation time equal to the niobium spin-lattice relaxation time: $\tau_c = T_1Nb$. The probability for induced relaxation transitions[11] is given by

$$P(\omega) = \frac{1}{\hbar^2} |\bar{V}|^2 \frac{2\tau_c}{1 + (\omega_{Al} - \omega)^2 \tau_c^2}, \tag{5}$$

(ω_{Al} and ω are the aluminum and niobium Larmor frequencies), and will be important only when $\omega \approx \omega_{Al}$. If the niobium NMR spectrum is described by the frequency density distribution function $g(\omega)$ and its dipole contribution to the aluminum line width is H_d, the ^{27}Al spin-lattice cross relaxation rate will be

$$\frac{1}{T_{1 \, cross}} = \gamma_{Al}^2 |\bar{H}_d|^2 \int_0^\infty \frac{\tau_c g(\omega) d\omega}{1 + (\omega_{Al} - \omega)^2 \tau_c^2}. \tag{6}$$

In evaluating the integral in (6) we need consider only frequencies of the order of 10^4 Hz close to ω_{Al}. In this narrow frequency range we have $g(\omega) \approx g(\omega_{Al})$ = $0.6g(\omega_{Nb}) = 0.3 \times 10^{-6}$ Hz^{-1} for $Nb_3Al_{1-x}Ge_x$ specimens with $x < 0.5$. The niobium contribution to the dipole width of the aluminum line is $|\overline{H}_d|^2 \approx 4-9$ G^2, and $\tau_c \approx 10^{-3}$ sec at 78° K. In this case $T_{1\,cross} = 380-150$ msec, while the experimental value of T_1 after subtracting the electron contribution (4) is 270 msec. This shows that cross relaxation may play an important part. This is confirmed by measurements on an $Nb_3Al_{0.25}Ge_{0.75}$ specimen for which the lines overlap more and the ^{93}Nb NMR spectrum is such that $g(\omega_{Al}) \approx 0.9g(\omega_{Nb})$. In this case the longitudinal relaxation time should be shorter, as experiment shows it to be.

B. The ^{27}Al NMR line shape

A low-temperature martensitic transformation accompanied by a slight tetragonal deformation of the cubic lattice without volume change has been discovered in certain compounds with the A-15 structure (V_3Si, Nb_3Sn, and others) and it has been shown that this transformation leads also to changes in the NMR spectrum. The NMR lines of ^{51}V in V_3Si and ^{93}Nb in Nb_3Sn undergo additional quadrupole splitting and an asymmetric shift below a certain temperature[12]. Whereas the tetragonal deformation in V_3X compounds (X = Si, Ga, Ge) and Nb_3Sn has been confirmed by many investigators, no such deformation has been detected in $Nb_3Al_{1-x}Ge_x$ alloys[2,7]. We undertook special measurements of the aluminum NMR shape, but in none of the investigated specimens (both powders and bulk $Nb_3Al_{0.75}Ge_{0.25}$ specimens) was there observed any additional splitting of the ^{27}Al line at 20.4° K. A 4 G broadening of the ^{119}Sn line in Nb_3Sn has been observed[7] below the martensitic transformation temperature of this compound ($T_m \approx 40°$ K). For all the investigated $Nb_3Al_{1-x}Ge_x$ alloys with $x < 0.4$, the width of the ^{27}Al line as determined from the extrema of the derivative is 8.5 ± 0.5 Oe and remains constant (within 0.5 Oe) over the entire temperature range from 20 to 200° K. These results provide grounds for asserting that it is unlikely that there is any tetragonal distortion of the A-15 lattice of $Nb_3Al_{0.75}Ge_{0.25}$, and that if there is such distortion, it has not been detected yet.

The NMR line shape for ^{27}Al in Nb_3Al and $Nb_3Al_{0.8}Ge_{0.2}$ specimens was investigated by both continuous and pulse methods. The free-induction drop for Nb_3Al at 20.4° K has a good Gaussian shape with the characteristic time $T_2^{*\prime} = 73.0 \pm 1.5$ μsec. The moment ratio $S_4/S_2^2 = 2.3$ also indicates a Gaussian line shape. The echo in a uniform magnetic field has a complex structure corresponding to three almost Gaussian signals with the characteristic times $T_2^{*\prime} = 76 \pm 2$ μsec, $T_2^{*\prime\prime} = 10.6 \pm 0.8$ μsec, and $T_2^{*\prime\prime\prime} = 4 \pm 0.8$ μsec. The induction drop undoubtedly also has a similar structure, but the fast processes could not be observed because of the receiver dead time. All the echo parameters remained constant as the temperature was raised to 78° K, but $T_2^{*\prime\prime}$ and $T_2^{*\prime\prime\prime}$ were about 1.7 times longer at 300° K. The reason for the growth of the fast echo components is not yet clear. At 78° K, $T_2^{*\prime\prime}$ and $T_2^{*\prime\prime\prime}$ are some 15-20% shorter for $Nb_3Al_{0.8}Ge_{0.2}$ than for Nb_3Al. This corresponds to larger stresses and lattice inhomogeneities in the ternary system than in the binary one.

The behavior of the ^{27}Al signal described above can be treated as nonuniform splitting of the line by the first-

order quadrupole interaction. The echo components with different time constants T_2^* correspond to different transitions: $T_2^{*\prime}$ to the transition $1/2 \rightarrow -1/2$, $T_2^{*\prime\prime}$ to the transition $\pm 3/2 \rightarrow \pm 1/2$, and $T_2^{*\prime\prime\prime}$ to the transition $\pm 5/2 \rightarrow \pm 3/2$. The rms value of the quadrupole coupling constant for ^{27}Al in Nb_3Al as determined from $T_2^{*\prime\prime}$ and $T_2^{*\prime\prime\prime}$ is 0.24 ± 0.06 MHz. It was difficult to observe the wings of the line using the continuous measurement method because the nonuniformity of the splitting tends to smear out the satellite structure.

C. The ^{93}Nb line shape

Unlike the corresponding vanadium compounds, niobium compounds with the A-15 structure have long resisted efforts to detect NMR signals from the group-V element. This is due to the large quadrupole broadening of the line. In 1970, however, there appeared a communication[13] in which observation of a narrow (down to 12 Oe) niobium line in Nb_3X compounds with X = Pt, Au, Os, Ir was reported. It was therefore natural to seek a similar line in $Nb_3Al_{0.75}Ge_{0.25}$. Measurements by the continuous method revealed ^{93}Nb lines (width ~ 28 Oe) from only two specimens out of the many examined. X-ray diffraction studies of the specimens showed that the two from which ^{93}Nb NMR signals were detected contained more of the σ phase than the others. The prolonged accumulation technique used in [13] apparently made it possible to detect signals from very small quantities of extraneous phases.

We used the spin echo technique to detect the NMR of ^{93}Nb nuclei lying on (6c) chains. As was done in [7], we recorded the part of the Nb_3Al NMR spectrum in the range of magnetic field strengths from 3 to 13 kOe. The spectrum is shown in Fig. 4 (for simplicity the aluminum line has been omitted and the corresponding part of the spectrum is shown dashed); it contains four prominent peaks. The theory of quadrupole effects up to the third order [14] must be invoked in order to identify the peaks. The ^{93}Nb quadrupole coupling constant was calculated directly from the measured quadrupole resonance frequencies. The frequencies 9.42 ± 0.06, 14.1 ± 0.1, and 18.7 ± 0.1 MHz correspond to the $\pm 3/2 \rightarrow \pm 5/2$, $\pm 5/2 \rightarrow \pm 7/2$, and $\pm 7/2 \rightarrow \pm 9/2$ transitions with the constant $e^2qQ/h = 112.7 \pm 0.5$ MHz. Our value of the constant differs somewhat from that obtained in [7], apparently because the higher-order corrections were neglected in that study.

When the aluminum in Nb_3Al is partly replaced by germanium, the satellite structure of the ^{93}Nb NMR line is no longer resolved. Figure 5a shows such a line; it
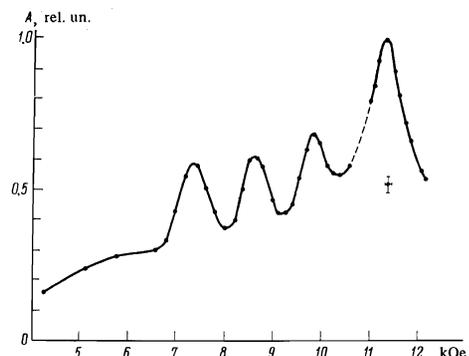
FIG. 4. NMR spectrum of ^{93}Nb in Nb_3Al at 78°K (A is the echo amplitude).

N. E. Alekseevskiĭ et al.
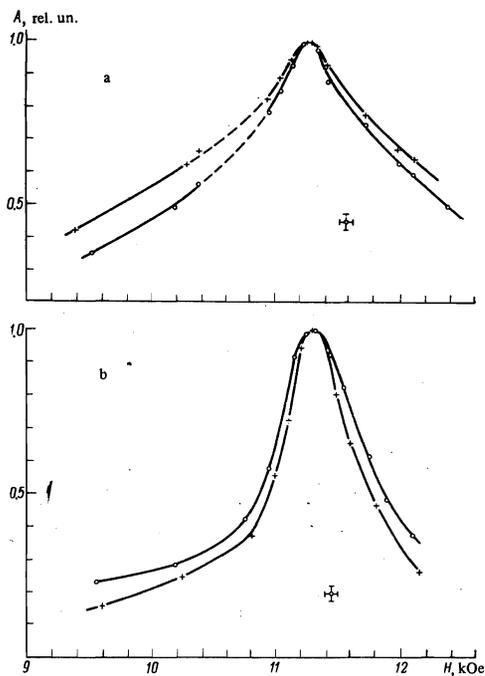
FIG. 5. NMR spectrum at 78°K of ^{93}Nb in $Nb_3Al_{0.8}Ge_{0.2}$ (a) and Nb_3Ge (b), before (crosses) and after (circles) annealing.

Safin for assistance with the quadrupole resonance frequency measurements.

has broad wings and a comparatively sharp peak (the part of the spectrum where the aluminum line would appear is shown dashed). Annealing $Nb_3Al_{1-x}Ge_x$ specimens with $x < 0.5$ narrowed the niobium line, whereas annealing Nb_3Ge specimens broadened the line (Fig. 5b). The effect of annealing on the spectrum is confirmed by measurements of the uniform spin-spin relaxation time from the decrement of the echo envelope. The relaxation time T_2^* is 10% longer for a cast $Nb_3Al_{0.8}Ge_{0.2}$ specimen than for a heat-treated one. These results provide a qualitative explanation for the "improvement" of the lattice following heat treatment, i.e., the relief of internal stresses and the reduction of the number of dislocation and defects, which, in turn, reduce the electric field gradients and lead to a narrowing of the NMR spectrum.

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32