Investigation of ternary molybdenum chalcogenides using NMR of ^{119}Sn

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The NMR spectra of ^{119}Sn were obtained in the superconducting compounds Mo_6S_8Sn and Mo_6Se_8Sn at $T \gtrsim T_c$. The observed line shape can be attributed to the structural singularities of these systems. The obtained results are discussed, with particular attention focused on the large isotropic Knight shift.

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An interest in superconducting ternary molybdenum chalcogenides with a chevrel-phase structure[1] is attributable to relatively high super-conducting-transition temperatures, large critical magnetic fields H_{c2} and large critical currents in these systems.[2] These compounds have a rhombohedral structure ($\bar{R}3$ symmetry), whose formula is $Mo_6X_8M_x$, where M is a metal atom and X is S, Se, Te. It was established that the superconducting properties of these systems depend strongly on the M atom.[2] It was of interest to investigate these compounds using nuclear magnetic resonance of the nucleus of an M atom.

We have investigated the NMR spectra of ^{119}Sn in the compounds MoS_8Sn($T_c = 12$ K) and Mo_6Se_8Sn ($T_c = 3.2$ K) using a stationary NMR spectrom-

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TABLE 1.

compound	T_c, K	K_{iso}, %	K_{an}, %	ΔH, Oe	χ ($T \gtrsim T_c$), cm³/g $\times 10^{-6}$
Mo_6S_8Sn	12	1,76	—	58	0,52
Mo_6Se_8Sn	3,2	0,62	0,09	24	0,55

eter with a supeconducting magnet analogous to that in Ref. 3. To increase the signal-to-noise ratio, we used polycrystalline samples prepared according to the method of Ref. 4 using ^{119}Sn isotope-enriched tin. The spectra were recorded by using an LP-4840 multichannel analyzer as a storage device. The measurements were performed at temperatures above T_c in a 17.5-kOe field. We obtained at $T = 4.2$ K an ^{119}Sn spectrum for the Mo_6Se_8Sn compound with a characteristic asymmetric broadening due to an anisotropic contribution to the Knight shift. At $T = 16$ K, Mo_6S_8Sn has a much broader symmetric line.

The results of the measurements of NMR along with the data for the susceptibility of these compounds at $T \gtrsim T_c$ are presented in Table I. If the density of states of the s electrons in the Sn atom can be estimated from K_{iso}, assuming that the Knight shift is mainly due to the contact contribution, then we obtain the values for Mo_6S_8Sn and Mo_6Se_8Sn comparable to the total density of states in the molybdenum atom, which can be estimated from the coefficient of electron specific heat for these compounds.[5] It is very likely that additional contributions to the ^{119}Sn Knight shift in Mo_6S_8Sn and Mo_6Se_8Sn are considerable.

The anisotropic ^{119}Sn Knight shift measured in Mo_6Se_8Sn apparently has only an axial component, since a tin atom in these compounds is located on the three-fold axis. A much broader line width of ^{119}Sn in Mo_6S_8Sn, as compared with that of selenide, is partially attributable to the fact that, in contrast to selenide, a large delocalization of an Sn atom can occur in sulfide.[6]

During the preparation of this paper for publication, we were given the results of Ref. 7 in which the nuclear magnetic resonance of ^{207}Pb in Mo_6S_8Pb and Mo_6Se_8Pb compounds was investigated. The Knight shifts obtained in this investigation in the case of sulfides almost coincide with our results for ^{119}Sn and are comparable to them in the case of selenides. This is not surprising, since the systems have similar superconducting properties. Moreover, it was shown in Ref. 7 that the Korringa product for ^{207}Pb in Mo_6S_8Pb and Mo_6Se_8Pb has a very large value, which may be due to contributions to the Knight shift in addition to the contact contribution. As mentioned earlier, an analogous situation cannot be ruled out in Mo_6S_8Sn and Mo_6Se_8Sn. The line width of ^{207}Pb determined by Sano *et al.*[7] is 10 Oe for sulfide and selenide, which is much smaller than that of ^{119}Sn measured for Mo_6S_8Sn and Mo_6Se_8Sn in this investigation. An anisotropy of the Knight shift was not observed by Sano *et al.*,[7] possibly because of the inherent peculiarities of the spin-echo method used by them.

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