Temperature dependence of the NMR parameters of ^{119}Sn in the Mo_6S_8Mn compound

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The nuclear magnetic resonance of ^{119}Sn in the superconducting compound Mo_6S_8Mn has been investigated in the temperature range of 15 to 120 K. The observed variation of the NMR line width is explained by means of the diffusion narrowing mechanism. The relationship between the obtained results and the possibility of structural transformation in the system studied is discussed.

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Superconductors with high critical parameters are characterized by the presence of lattice instability, which is usually evident as a structural transition in the range of 20 to 150 K. In this case, as a rule, a softening of the phonon modes occurs and a change in the electron-phonon interaction is possible. One example of such an in-

stability is the martensitic transformation in compounds with an A-15 structure. Structural transformations are also observed in some superconducting Chevreul phases. For example, in the compound $Mo_6S_8Cu_{1.8}$ at 269 K a transition occurs from the rhombohedral structure above T_m to the triclinic structure at low temperatures.[1]

The possibility of a structural transition has been discussed repeatedly for the compound Mo_6S_8Sn. As a result of x-ray studies, it has been established that the rhombohedral structure is retained in this system down to 4.2 K,[2] although a broadening of the individual diffraction maxima has been observed. The temperature dependences of the electrical resistance, of the magnetic susceptibility and of the specific heat also exhibit no anomalies that can be attributed to a structural transformation. However, a study of the Mössbauer effect in ^{119}Sn nuclei in Mo_6S_8Sn showed that the temperature dependences of the isomer shift and of the ratio of the intensities of the quadrupole components of the spectrum have singularities in the temperature range 50–110 K.[2] In this paper it was assumed that a transition can occur in the system in which the relative arrangement of atoms in the unit cell is altered. The results of a study of the inelastic scattering of neutrons in the compounds Mo_6S_8Pb and Mo_6S_8Sn, in which a softening of the low-frequency phonon modes was observed in these systems with a decrease of the temperature,[3] also indicate the possibility of a transformation.

In our work we have investigated the temperature dependence of the parameters of the nuclear magnetic resonance absorption line of ^{119}Sn in the compound Mo_6S_8Sn. We have pointed out previously[4] that the large width of the resonance line of tin (~60 Oe) in this system at 15 K can be attributed in part to the delocalization of the Sn atom. The relationship between the delocalization of the third component in Chevreul phases and the structural instability of these systems was indicated in Ref. 5. Therefore, it was interesting to investigate how these effects manifest themselves on the temperature dependence of the NMR parameters of ^{119}Sn.

The measurements were carried out on a stationary NMR spectrometer, which was used in Ref. 4, in the temperature interval from 15 to 120 K on samples that contained tin enriched with the ^{119}Sn isotope. Figure 1 shows the temperature dependences of the width and the Knight shift of the tin line in the Mo_6S_8Sn compound. The line width is defined as the distance between the extrema of the derivative of the absorption line, and the zero point of the derivative was used to determine the shift beyond the center of the line. It can be seen in this figure that the width of the resonance line decreases considerably with increasing temperature. Measurements at 295 K showed that the width of the resonance line at this temperature is only 9 Oe. If it is assumed that the tin atoms start to migrate in the Mo_6S_8Sn lattice with an increase in temperature, then we can explain the observed change in the line width by means of the diffusion-narrowing mechanism.[6] As is known, a narrowing of the NMR line occurs as a result of diffusion if the time τ_c an atom spends in a given lattice site is less than the transverse relaxation time of the nuclear spins. Figure 2 shows the dependence of the logarithm of τ_c on the reciprocal of the temperature for the tin atom, which was calculated from the change in the NMR line width in accordance with the results of Ref. 6. At a temperature of the order of 80 K an abrupt change occurs in the slope of the log τ_c dependence; within the framework of our as-

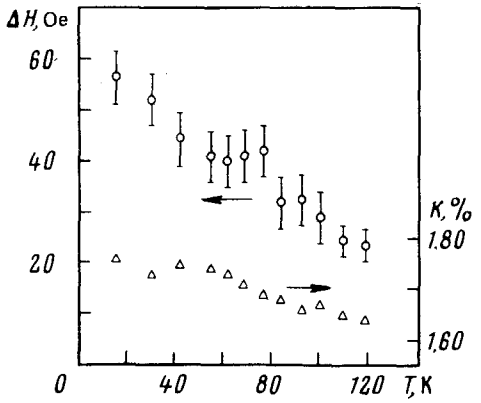

FIG. 1. Temperature dependences of the Knight shift (Δ) and line width (○) of the NMR of ^{119}Sn in the Mo_6S_8Sn compound. The measurements were carried out in a 16.2-kOe field.

sumption, this may be construed as an indication of the presence of two activation energies for the tin migration. As is known, the activation energy E_a is determined from the slope of the dependence of $\log \tau_c$ on the reciprocal temperature in accordance with the expression $\tau_c = \tau_{c0} \exp(E_a/kT)$. The activation energies obtained in this manner amount to $(3 \pm 2) \times 10^{-3}$ eV in the temperature range 15–80 K and $(2 \pm 0.5) \times 10^{-2}$ eV for temperatures higher than 80 K.

The migration of a tin atom in the system under investigation is determined by the fact that the ternary molybdenum chalcogenides are inclusion compounds, in which the third component is located in channels between the Mo_6S_8 clusters and is bound relatively weakly to the rest of the lattice. It was pointed out elsewhere[7] that several equivalent positions of the Sn atom can exist at a distance of the order of 0.1 Å (amount of delocalization) from the (0, 0, 0) location, in analogy with the copper atoms in the $Mo_6S_8Cu_x$ system. It is natural to assume that, as the temperature is increased, the tin atoms first migrate with respect to these positions, and the acti-

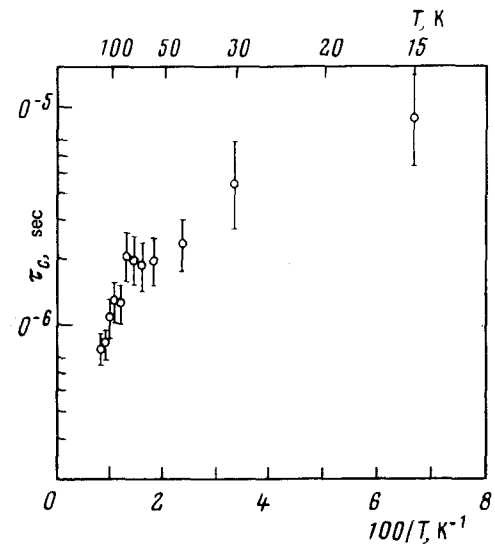

FIG. 2. Dependence of the logarithm of τ_c for tin atoms on the reciprocal temperature in the Mo_6S_8Sn compound.

vation energy in the temperature range 15–80 K characterizes the energy barrier between these positions. The large anharmonicity of the vibrations of Sn atoms mentioned in Ref. 2 also favors this possibility. The presence of large anharmonicity, in turn, can explain the anomalous isotopic effect in tin in this superconducting system.[8]

At temperatures above 80 K a greater migration of tin atoms, which is characterized by a larger activation energy, is possible. This is consistent with the decrease in magnitude of the Knight shift in this temperature region. If the Sn atom spends some time near the $(\frac{1}{2}, 0, 0)$ location, then an increase of the overlap between the tin electrons and the molybdenum *d* orbitals is possible; this can lead to a negative contribution to the Knight shift. A displacement of molybdenum and sulfur atoms can probably occur at temperatures of the order of 80 K without a significant change in the lattice parameters, but the position of tin atoms and hence the activation energy may change. For example, this may appear as an increase of the rotation of Mo_6S_8 clusters about the third-order axis or a slight compression of the lattice along this direction.[2] The displacement of atoms in the Mo_6S_8Sn lattice could be attributed to the existence of a charge-density wave below 80 K, which may change the NMR line width.[9]

Other explanations of line narrowing with increasing temperature should not be ruled out. For example, it may be caused by a dissipation of small triclinic distortions of the lattice. It can be assumed that the observed singularities of the temperature dependences of the Knight shift and NMR line width of ^{119}Sn in the Mo_6S_8Sn compound are caused by a possible transformation of this system.

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