

Knight shift of ^{119}Sn in $\text{Mo}_6\text{S}_8\text{Sn}$

N. E. Alekseevskii and E. G. Nikolaev

Institute of Physical Problems, Academy of Sciences of the USSR

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The temperature and pressure dependence of the Knight shift of ^{119}Sn in the compound $\text{Mo}_6\text{S}_8\text{Sn}$ has been measured. The relationship between the results and the temperature dependence of the magnetic susceptibility of this compound is discussed.

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A study of the nuclear magnetic resonance of ^{119}Sn nuclei in molybdenum chalcogenides with the Chevrel-phase structure was reported in Refs. 1 and 2. The shape of the NMR line in sulfides and selenides of molybdenum with tin was discussed there, and the temperature dependence of the line width in the compound $\text{Mo}_6\text{S}_8\text{Sn}$ was studied. In the present letter we report a study of the temperature dependence of the Knight shift of ^{119}Sn in $\text{Mo}_6\text{S}_8\text{Sn}$ between 15 and 300 K and the temperature dependence of the susceptibility of this system. We also report results on the effect of pressure on the Knight shift of ^{119}Sn in this system. The pressure effect is of interest in connection with the strong pressure dependence of the superconducting properties of Chevrel phases.³ For the NMR measurements we used the ^{119}Sn -enriched samples which were used previously in Ref. 2. The spectra were recorded with a steady-state autodyne NMR spectrometer with a superconducting magnet⁴ with data accumulation in a multichannel analyzer. For the NMR measurements under pressure, the rf circuit with the sample was placed inside a beryllium bronze bomb, in which the pressure could be raised to 10 kbar. In determining the Knight shift K we used as a reference sample a small aluminum sample in the circuit beside the test sample (the Knight shift of ^{27}Al changes by no more than 0.001% at a pressure of 5 kbar). The susceptibility was measured by the Faraday method with a magnetic balance.

Figure 1 shows the temperature dependence of the Knight shift of ^{119}Sn in the compound $\text{Mo}_6\text{S}_8\text{Sn}$. We first note that the shift decreases essentially linearly at temperatures below 50 K. In general, the temperature dependence of the Knight shift can

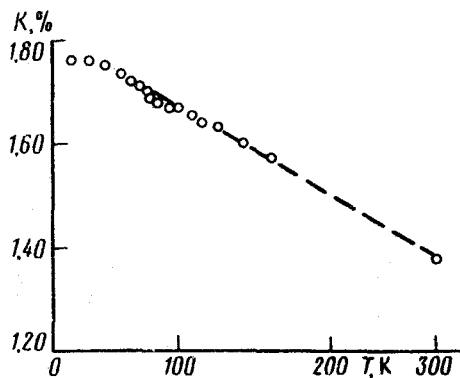


FIG. 1. Temperature dependence of the Knight shift of ^{119}Sn in the compound $\text{Mo}_6\text{S}_8\text{Sn}$. The measurements were taken in a 11.7-kOe field.

be described by

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{(\partial \ln K / \partial p)_T (\partial \ln V / \partial T)_p}{(\partial \ln V / \partial p)_T} + (\partial \ln K / \partial T)_V. \quad (1)$$

The first term on the right side of Eq. (1) describes the change in the Knight shift due to thermal expansion. The second term describes the temperature dependence at a constant volume. Our measurements of the Knight shift of ^{119}Sn in $\text{Mo}_6\text{S}_8\text{Sn}$ under pressure at temperatures of 20, 77, and 86 K show that at 6 kbar the shift changes by no more than 0.02%. The quantity $|(\partial \ln K / \partial p)_T|$ thus does not exceed $2 \times 10^{-3} \text{ kbar}^{-1}$. Webb and Shelton⁵ found a value of $-2 \times 10^{-3} \text{ kbar}^{-1}$ for $(\partial \ln V / \partial p)_T$ for $\text{Mo}_6\text{S}_8\text{Sn}$, while Alekseevskii *et al.*⁶ found $-3 \times 10^{-4} \text{ kbar}^{-1}$. If we adopt the value $(\partial \ln V / \partial T)_p = 1.4 \times 10^{-5} \text{ kbar}^{-1}$ for this system over the temperature range from 50 to 100 K (Ref. 7), we find that the absolute value of the first term on the right side of Eq. (1) is less than $10^{-4} \text{ kbar}^{-1}$. The value of $(\partial \ln K / \partial T)_p$ found from the temperature dependence of the Knight shift is $-1.0 \times 10^{-3} \text{ kbar}^{-1}$ between 50 and 100 K. It can thus be concluded that the temperature dependence of the Knight shift is determined by the second term in Eq. (1), which represents the temperature-induced change in the electron system which is unrelated to the change in volume.

The magnetic susceptibility of $\text{Mo}_6\text{S}_8\text{Sn}$, like the Knight shift, is a linear function of the temperature above 50 K. Below 30 K, there is a slight increase in the susceptibility, apparently due to a small magnetic impurity in the sample.¹⁾ We see from Fig. 2, which shows the χ dependence of K between 50 and 300 K, that the shift varies approximately in direct proportion to the magnetic susceptibility. In most cases the Knight shift depends linearly on the susceptibility, but systems with transition metals usually do not exhibit a direct proportionality.⁸ There are also cases of a nonlinear relationship between the Knight shift and the susceptibility. The susceptibility of $\text{Mo}_6\text{S}_8\text{Sn}$ can be written

$$\chi = \chi_p + \chi_{uv} + \chi_{\text{dia}}, \quad (2)$$

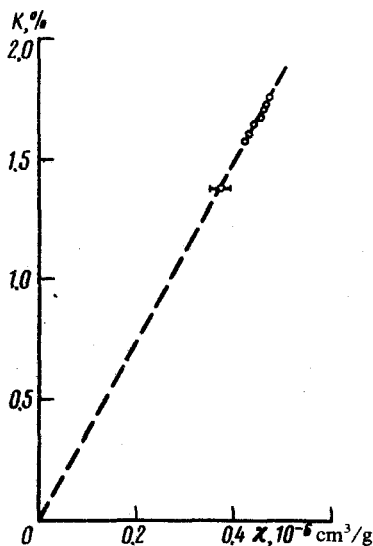


FIG. 2. Dependence of the Knight shift of ^{119}Sn in $\text{Mo}_6\text{S}_8\text{Sn}$ on the magnetic susceptibility.

where χ_p is the Pauli susceptibility of the conduction electrons, χ_{vv} is the orbital susceptibility of the conduction electrons, and χ_{dia} is the diamagnetic susceptibility of the ion lattice. Landau diamagnetism can usually be ignored in transition metals and their compounds because of the large effective mass of the current carriers. The contributions in the Knight shift are similar. The diamagnetic contribution, however, is usually two orders of magnitude smaller than the total shift. The orbital contribution is usually also small for nontransition elements. It may thus be assumed that the only important component of the Knight shift of ^{119}Sn in $\text{Mo}_6\text{S}_8\text{Sn}$ is χ_p . In view of the proportionality of the shift to the susceptibility, we can assume in our case that the susceptibility of $\text{Mo}_6\text{S}_8\text{Sn}$ is also determined primarily by the Pauli component. It may be that in this case χ_{vv} and χ_{dia} cancel out to a large extent, in contrast with the A-15 compounds, where the orbital component of the susceptibility is considerably greater than the diamagnetic component.⁸ We do not rule out the possibility that a cancellation of this type is characteristic of any Chevrel phases.

Using $\chi_p = 2\mu_B^2 N(0)$ we can estimate the state density for the compound $\text{Mo}_6\text{S}_8\text{Sn}$. At 50 K we find $N(0) = 1.1 \pm 0.4$ [eV (Mo atom) spin]⁻¹. The indicated error in $N(0)$ means that we cannot rule out a slight effect of a small magnetic impurity on the temperature dependence of the susceptibility (as discussed above). If we use the electron specific heat $\gamma = 84$ mJ/mole K²) and the electron-phonon interaction constant $\lambda = 1.44$ which were found for $\text{Mo}_6\text{S}_8\text{Sn}$ in Ref. 10, we find $N(0) = 1.2$ [eV (Mo atom) spin]⁻¹, in good agreement with the value which we found for the state density. We should point out that γ_0 was estimated from the value of χ for $\text{Mo}_6\text{S}_8\text{Sn}$ in Ref. 10. When we multiply this value by $(1 + \lambda)$ we again find a good agreement with the measured specific heat.

A linear temperature dependence of the susceptibility has also been observed for

other molybdenum chalcogenides having high critical parameters, $\text{Mo}_6\text{Se}_8\text{La}$, for example.¹¹ This behavior seems to be characteristic of Chevrel phases having a high state density at the Fermi level. In conclusion, we should point out that the small pressure-induced change in the Knight shift of ^{119}Sn in $\text{Mo}_6\text{S}_8\text{Sn}$ which we have found means that the large value of $\partial T_c/\partial p$ of the system cannot be attributed to a change in the state density during hydrostatic compression.

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¹¹According to an activation analysis, the iron concentration in these samples did not exceed 0.01 at.%.

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