

## Peculiarities of the isotopic effect in $\text{SnMo}_6\text{S}_8$

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The isotopic effect is investigated in  $\text{SnMo}_6\text{S}_8$  samples using  $\text{Sn}^{112}$  and  $\text{Sn}^{124}$  tin isotopes  $\text{Mo}^{92}$  and  $\text{Mo}^{100}$  molybdenum isotopes. In the case of molybdenum, the isotopic effect has a normal sign. The data obtained for the tin isotopes lead to the assumption that  $\partial T_c / \partial M > 0$ .

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As is known, the ternary molybdenum chalcogenides of the  $\text{AxMo}_6\text{S}_8$  compound, in addition to having record values of  $H_{c2}$ <sup>(1)</sup> and high critical current densities, exhibit a complex phonon spectrum.<sup>(2-4)</sup> It was assumed by Alekseevskii *et al.*<sup>(5)</sup> that these compounds may be regarded as inclusions, in which a system of  $\text{Mo}_6\text{S}_8$  clusters—"host molecules"—is a certain kind of "inorganic polymer," and the  $A$  atoms in the voids between the clusters are "guest" atoms. They also pointed out that if  $T_c$  is plotted as a function of the atomic weight  $A$ , then the isoivalent  $A$  atoms will have smooth  $T_c(M_A)$  dependences, where  $M_A$  is the mass of the  $A$  atoms.

These dependences may be regarded, in a certain sense, as an inverse isotopic effect similar to that observed in palladium hydride and deuteride.

In view of this, it was of interest to carry out direct investigation of the effect of the atomic mass  $M_A$  on the critical temperature of molybdenum sulfide. The most suitable material for this investigation apparently is the  $\text{SnMo}_6\text{S}_8$  compound, which can be easily synthesized and is sufficiently stable, whereas tin has five isotopes whose mass differs substantially.

First, we measured the critical temperature  $T_c$  of the  $\text{Sn}^{112}\text{Mo}_6\text{S}_8$  and  $\text{Sn}^{124}\text{Mo}_6\text{S}_8$  samples and of the samples containing natural isotopic tin.

To determine the effect of preparation on  $T_c$  of  $\text{SnMo}_6\text{S}_8$ , we prepared two batches of samples from ordinary, non-monoisotopic components; the maximum deviation of  $T_c$  from the average value did not exceed 0.07 K. The samples were prepared by direct synthesis of the components in a quartz flask filled with pure helium gas. After the synthesis, the samples were ground in an agate mortar and then pressed at a pressure  $P \sim 15\text{--}30$  Torr into 2-mm-diam, 5-mm-long cylinders and were annealed. The annealing was performed at  $T \approx 1000^\circ\text{C}$ ; the annealing time for the first three batches was 24 hours. The measurements of  $T_c$  was first conducted using three batches of  $\text{Sn}^{112}\text{Mo}_6\text{S}_8$  and  $\text{Sn}^{124}\text{Mo}_6\text{S}_8$  samples. The preparation of all the samples was maintained as constant as possible. The  $T_c$  was determined from the variation of the resistance. Two samples were measured simultaneously. The temperature was measured with the TGS-2 germanium thermometer calibrated to an accuracy within 0.05 K. The transition curves were recorded by a two-arm "BRYANS" X-Y automatic recorder. A signal from the potential terminals of the sample was preamplified by a R-325 amplifier. The measuring assembly whose output connected to a perforator, was connected in parallel with the automatic recorder. The punch cards were processed on a computer and a plotting device was used to obtain the averaged transition curves.

In view of the fact that the first two batches of tin isotopes contained unequal amounts of iron impurities (a difference of several hundredths of one percent), a correction for the iron content was introduced in determining the critical temperature of molybdenum sulfides that were prepared from these tin samples. For this purpose, we used the known data for the dependence of  $T_c$  on the Fe content.<sup>16)</sup> This correction was not needed for the remaining series of samples, since the concentration of Fe in Sn was  $\leq 0.001\%$ .

The measurements of the first three batches of the  $\text{Sn}^{112}\text{Mo}_6\text{S}_8$  and  $\text{Sn}^{124}\text{Mo}_6\text{S}_8$  samples (see Table I) indicate that the samples containing  $\text{Sn}^{124}$  go superconducting at little higher temperatures than that of the samples containing  $\text{Sn}^{112}$ ; moreover,  $\Delta T_c$  was  $\leq 0.4$  K and average value of  $\beta^{(1)}$  was  $\langle \beta \rangle = 0.4 \pm 0.1$ . The measurements of the

Table I

Series	$\text{Sn}^{112}\text{Mo}_6\text{S}_8$	$\text{Sn}^{124}\text{Mo}_6\text{S}_8$	$\Delta T_c = (T_c)_{124} - (T_c)_{112}$
1	11.91	12.33	0.42
2	12.10	12.56	0.46
3	12.08	12.54	0.46
4	13.41	13.80	0.39
5	13.01	13.32	0.31
6	11.56	11.68	0.12
7	11.52	11.67	0.15

critical temperature of the samples containing different molybdenum isotopes,  $\text{SnMo}_6^{92}\text{S}_8$  and  $\text{SnMo}_6^{100}\text{S}_8$ , showed that in this case the  $T_c$  of the samples with light molybdenum isotope  $\text{Mo}^{92}$  exceeds the  $T_c$  of the sample with  $\text{Mo}^{100}$ ; i.e., in this case the normal isotopic effect is in effect, which is similar to that observed in the  $\text{Mo}_6\text{S}_8$  compound<sup>(7)</sup>; the value of  $\beta$  for the Mo isotopes was  $\langle \beta \rangle = -0.48 \pm 0.1$ . Unfortunately, further measurements performed with other batches of samples containing  $\text{Sn}^{112}$ ,  $\text{Sn}^{116}$ ,  $\text{Sn}^{119}$ ,  $\text{Sn}^{120}$ , and  $\text{Sn}^{124}$  failed to confirm the first results. The spread of the experimental points in these tests was sufficiently large. The obtained data supported Culetto's<sup>(7)</sup> assumption that, because of a weak overlapping of the Mo  $d$  orbitals with Sn atoms, the isotopic effect in Sn is equal to zero, which, in his opinion, is confirmed by his experimental data. However, additional experiments performed with several series of  $\text{SnMo}_6\text{S}_8$  helped to establish the following: if the annealing time is insufficiently long for the preparation of the samples or it occurs at a temperature below  $1000^\circ\text{C}$ , the dispersion of the  $T_c$  of the obtained samples is rather large. However, prolonged ( $\sim 100$  hours) or repeated annealing decreases the dispersion of  $T_c$ . This result agrees, for example, with the results for  $\text{PbMo}_6\text{S}_8$  and for certain other molybdenum sulfides obtained in Ref. 8, where the dependence of  $T_c$  on the bulk of the unit cell was investigated and where it was established that  $T_c$  of the different samples approaches a constant value as a result of prolonged annealing. Less contradictory data were obtained when five additional series of samples with different tin isotopes were subjected to a long annealing process. Table I gives  $T_c$  values for the  $\text{Sn}^{112}\text{Mo}_6\text{S}_8$  and  $\text{Sn}^{124}\text{Mo}_6\text{S}_8$  samples from these series. We can conclude from the given data, with greater probability that an inverse sign of the isotopic effect is observed in the  $\text{SnMo}_6\text{S}_8$  compound; moreover, the average value of  $\langle \beta \rangle$  obtained from the data for one of the series of samples is  $0.14 \pm 0.07$ . If we use the data for  $\Delta T_c$  obtained for all seven series of samples subjected to prolonged annealing, then  $\langle \beta \rangle = 0.23 \pm 0.04$ . It should be noted that, contrary to the author's assertions, the data of Ref. 9 confirm this viewpoint.<sup>2)</sup>

If we assume that an anomalous isotopic effect actually occurs in the Sn atoms of the  $\text{SnMo}_6\text{S}_8$  compound, then it can be regarded as an analog of the anomalous isotopic effect in the Pd- $H$ ,  $D$  system. As is well known, the opposite sign of the isotopic effect in the latter case is attributable to a strong vibrational anharmonicity of the light-component atoms.<sup>(10)</sup> Our preliminary experiments on the effect of pressure on the isotopic effect in  $\text{SnMo}_6\text{S}_8$  showed that it decreases in the case of close compression. This pressure effect can evidently be regarded as an indirect indication of the key role of anharmonicity in  $\text{SnMo}_6\text{S}_8$ . It should be pointed out that an explanation of the anomalous isotopic effect in terms of anharmonicity is not unique; for example, the variation of the electronic band structure of Pd- $H$ ,  $D$  with the mass of the hydrogen isotope was examined in Ref. 11.

The results obtained in this work show that the behavior of the  $\text{Mo}_6\text{S}_8$  complexes differs greatly from that of the atoms of the third component—in this case Sn. This difference can determine to a large extent the properties of molybdenum sulfides in superconducting and in the normal states.

<sup>1)</sup>As is known,  $T \sim M^{-\beta}$ .

<sup>2</sup>If we assume that the point on the lower right-hand side of Fig. 11 in Ref. 9 is erroneous and estimate  $\langle \beta \rangle$ , then it turns out that  $\langle \beta \rangle = 0.16 \pm 0.07$ .

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