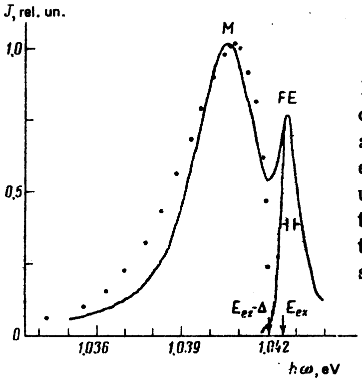

FIG. 6. Comparison of the calculated RR spectrum of a biexciton (points) with the experimental one. The figure shows also the RR spectrum of the exciton (FE) obtained at low excitation density. $T = 1.8$ K.

contour with the aid of a model-derived expression for the matrix element $M(\mathbf{P}|\mathbf{q}, \mathbf{Q})$, is logically contradictory. In fact, as seen from (7), both the line shape and the binding energy are uniquely determined by the wave function of the biexciton and are consequently not independent quantities. Thus, on the basis of the analysis of the shape it is impossible to determine exactly the true value of the biexciton binding energy.

Assuming thermodynamic equilibrium in the gas phase, the biexciton binding energy was estimated by us from the temperature dependence of the ratio of the exciton and biexciton line intensities in the interval $T = 2$ to 4.2 K and turned out to be $\Delta = 0.55 \pm 0.15$ meV.

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1) Secs. 2 and 5 were written by two of the authors (V. K. and V. T.), Sec. 6 by the third (V. E.), and Sec. 7 by all three of us.

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Critical magnetic fields of molybdenum chalcogenides

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The critical temperatures T_c and upper critical magnetic fields $H_{c2}(T)$ have been measured for a number of molybdenum sulfides prepared from Mo_6S_8Pb and Mo_6S_8Sn. It is shown that introduction of additional components into these compounds can lead to a simultaneous increase of T_c and $H_{c2}(0)$. The maximum critical field $H_{c2}(0) = 0.58$ MOe is observed in a specimen of the composition $Mo_6S_8PbGa_{0.4}W_{0.4}$, for which $T_c = 14.9$ K.

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Among the superconductors within the last decade, great interest attaches to systems in which the superconductivity is retained in superhigh magnetic fields. Such systems include, for example, molybdenum sulfide to which has been added a small amount of lead. Thus the compound of composition $Mo_{5.1}S_6Pb$ has a critical field $H_{c2}(0)$ exceeding 0.5 MOe.[1] It seemed of interest to conduct investigations of the upper critical fields H_{c2} of several new molybdenum chalcogenides, and also to repeat the measurements of such systems as Mo_6S_8Pb and to try to find a way of explaining the mechanism that leads to the occurrence of such high values of H_{c2}.

The measurements of H_{c2} were made in a pulse apparatus, which was constructed on the basis of one that had existed earlier.[2] The total capacitance of the capacitor band in the apparatus was 0.012 F, with operating voltage 5000 V. Upon discharge of the capacitors to a pulse solenoid, a magnetic field with amplitude in excess of 0.5 MOe was generated; the duration of the pulse was 0.01 sec. The destruction of superconductivity by the magnetic field was registered, as in Ref. 2, on the basis of the appearance of resistance. An alternating current, of frequency 4 kHz and amplitude 10 mA, was fed through the current electrodes to the specimen, and the signal taken from the potential electrodes was amplified and fed to an oscillograph with memory.

In a number of cases, an electrodeless method was used for registering the transition of the specimen from the superconducting to the normal state. Experimental test showed that the difference in the determination of H_{c2} by these two methods did not exceed 2%. Because insufficiently good thermal contact of the specimen with the cryoagent can lead to errors2) in the determination of H_{c2}, the specimen was not immersed in a stabilizing liquid, as was done earlier,[2] but was fastened mechanically to a holder.

We made measurements of the temperature dependence of H_{c2} on specimens of the following molybdenum sulfides:

Mo_6S_8Pb, $Mo_6S_8PbGa_{0.4}Re_{0.4}$, $Mo_6S_8PbGa_{0.4}W_{0.4}$,

$Mo_6S_8PbGa_{0.4}Ti_{0.4}$, Mo_6S_8Sn, $Mo_6S_8SnGa_{0.4}Re_{0.4}$,

$Mo_6S_8SnRe_x$, $MO_6S_8Sn_{1.2}Ga_x$, $Mo_5S_6SnFe_x$,

$Mo_6S_8SnNi_x$, $Mo_6S_8Sn_{1-x}Eu_x$, $Mo_6S_8SnYb_x$.

The specimens were prepared by a technology already described[3,4] and were cylinders of diameter 5 mm and length 10 mm. For the electrode measurements, specimens, whose dimensions usually were 5 × 1 × 1 mm, were cut from such cylinders; the current and potential electrodes were fastened to the specimens with silver conducting paste. For the electrodeless measurements, small pieces of the material under investigation, of volume from 1 to 5 mm^3, were used.

In the range 0 to 0.2 MOe, the measurements of H_{c2} were usually made in stationary magnetic fields, produced with a water-cooled solenoid of the Bitter type in the International Laboratory of Strong Magnetic Fields and Low Temperatures in Wroclaw, Polish People's Republic.

Figure 1 shows the functions $H_{c2}(T)$ for several of the specimens investigated. The ternary sulfide of molybdenum, of composition Mo_6S_8Pb, had $T_c = 14$ K, $(\partial H_{c2}/\partial T)_{max} = 50$ kOe/K, and $H_{c2}(0) = 0.55$ MOe. These data agree quite well with the results of Foner *et al.*[1] Investigations of four-component compounds based on Mo_6S_8Pb with additions of Ga and Gd showed that H_{c2} at $T \leqslant 4.2$ K is 4–5% lower in them than in the compound Mo_6S_8Pb.

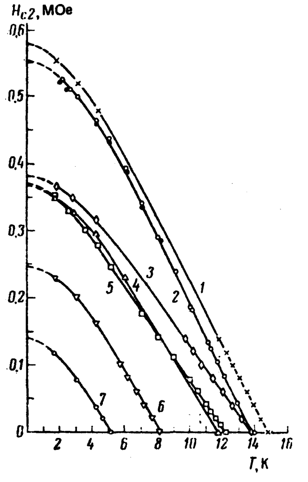

FIG. 1. Variation of the upper critical field H_{c2} with temperature T for several of the molybdenum sulfides investigated. The values of H_{c2} at fields up to 9.2 MOe and the dark circles on Curve 2 correspond to contact measurements. The remaining data were obtained by the electrodeless method. The curves correspond to: 1, $Mo_6S_8PbGa_{0.4}W_{0.4}$; 2, Mo_6S_8Pb; 3, $Mo_6S_8Sn_{1.2}Ga_{0.35}$; 4, $Mo_6S_8Sn_{1.2}$; 5, $Mo_6S_8Sn_{1.2}Ga_{0.05}$; 6, $Mo_5S_6SnFe_{0.01}$; 7, $Mo_6S_8PbGa_{0.4}Ti_{0.4}$.

The compound of composition $Mo_6S_8PbGa_{0.4}Re_{0.4}$ had $T_c = 14.4$ K, but it had $(\partial H_{c2}/\partial T)_{max} = 42$ kOe/K and $H_{c2}(0) = 0.52$ MOe; that is, the values were lower than in the ternary sulfide Mo_6S_8Pb.

The maximum critical field $H_{c2}(0) = 0.58$ MOe was observed in a specimen of $Mo_6S_8PbGa_{0.4}W_{0.4}$, which had $T_c = 14.9$ K and $(\partial H_{c2}/\partial T)_{max} = 46.5$ kOe/K. Replacement of W in this compound by Ti in the same amount led to a frop of T_c and H_{c2} (curve 7 in Fig. 1).

Another group of the specimens that we investigated was prepared from the compound Mo_6S_8Sn, which had $T_c = 11.7$ K, $(\partial H_{c2}/\partial T)_{max} = 37$ kOe/K and $H_{c2}(0) = 0.37$ MOe. It is seen from Fig. 2 that in the case of $Mo_6S_8SnRe_x$, the effect of Re on the superconducting parameters of the compound is very weak and begins to show up only when $x \geqslant 0.4$.

In the system $Mo_6S_8SnGa_x$, the values of T_c and H_{c2} at $T = 1.6$ K initially increase with increase of x, reach

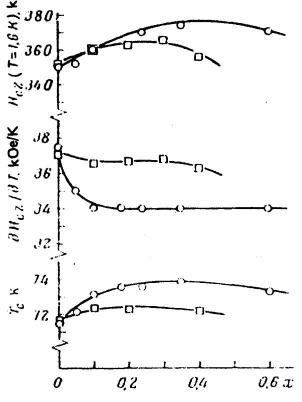

FIG. 2. Change of the superconductivity parameters T_c, $\partial H_{c2}/\partial T$, and H_{c2} at $T = 1.6$ K with content of the fourth component in the systems: ○, $Mo_6S_8Sn_{1.2}Ga_x$; □, $Mo_6S_8SnRe_x$.

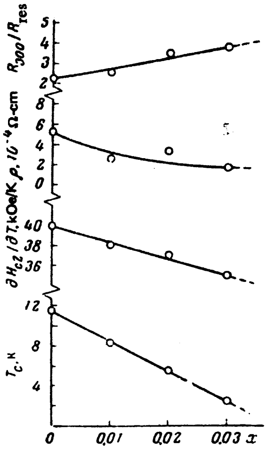

FIG. 3. Change of the residual electrical resistivity ρ, the ratio R_{300}/R_{res} of the resistance at $T = 300$ K to the residual, the temperature derivative $\partial H_{c2}/\partial T$ of the upper critical magnetic field near T_c, and the critical temperature T_c with iron content x in the system $Mo_5SnS_6Fe_x$.

a maximum at $x = 0.35$, and thereafter slowly drop. Introduction of atoms of the rare earths Yb and Eu into the compound Mo_6S_8Sn leads to an increase of the upper critical field to the value $H_{c2}(0) = 0.43$ MOe, while T_c remains practically constant.

Doping of the compound Mo_6S_8Sn with small amounts of ferromagnetic metals led to a pronounced lowering of the superconductivity parameters. As is seen from Figs. 1 and 3, in the system $Mo_5S_6SnFe_x$ there occurred, along with an abrupt drop of T_c,[6] a pronounced decrease of H_{c2}. A smoother decrease of the superconductivity parameters was observed in the system $Mo_6S_8SnNi_x$.

It follows from our results that introduction of additional components into the compound Mo_6S_8Sn or Mo_6S_8Pb may cause: (a) Simultaneous increase of T_c and $H_{c2}(0)$, with some decrease of $(\partial H_{c2}/\partial T)_{max}$ ($Mo_6S_8PbGa_{0.4}W_{0.4}$ and $Mo_6S_8SnGa_{0.35}$). (b) Increase of $H_{c2}(0)$ and $(\partial H_{c2}/\partial T)_{max}$, with a slight change of T_c ($Mo_6S_8SnYb_{0.3}$ and $Mo_6S_8Sn_{0.7}Eu_{0.3}$). (c) Increase of T_c, with simultaneous decrease of $(\partial H_{c2}/\partial T)_{max}$ and $H_{c2}(0)$ ($Mo_6S_8PbGa_{0.4}Re_{0.4}$). (d) Abrupt decrease of T_c and H_{c2} and a less pronounced drop of $(\partial H_{c2}/\partial T)_{max}$ ($Mo_5S_6SnFe_{0.01}$ and $Mo_6S_8SnNi_{0.01}$), (e) A very slight change of all three superconductivity parameters ($Mo_6S_8SnRe_x$, $x \leq 0.3$).

The most important result for the systems investigated must be regarded as the increase of T_c by almost 1 K and of $H_{c2}(0)$ by 0.025 MOe on introduction of Ga and W into Mo_6S_8Pb, and the abrupt decrease of $H_{c2}(0)$ and T_c on doping of Mo_6S_8Sn and Mo_5S_6Sn with small amounts of the ferromagnetic metals Fe and Ni. Along with this, it must also be noted that the rare-earths Eu and Yb, introduced as a fourth component into the compound Mo_6S_8Sn, leave T_c practically unchanged but lead to an increase of $H_{c2}(0)$. One of the possible explanations of such a behavior of $H_{c2}(0)$ is that in systems with rare earths, an important role is played by exchange interaction.[7]

It is also an interesting fact that in molybdenum sulfides containing nontransitional metals, magnetic ordering is observed, for example in Mo_5GaS_6.[8] It is possible that the occurrence of such ordering can explain why, in the specimen of $Mo_6S_8Sn_{1.2}Ga_{0.05}$, despite the decrease of $(\partial H_{c2}/\partial T)$ near T_c, the upper critical field H_{c2} at $T = 1.6$ K is the same as in the compound $Mo_6S_8Sn_{1.2}$ (Curves 5 and 4 in Fig. 1).

As was mentioned in Ref. 6, superconducting molybdenum chalcogenides containing lead or tin as a third component have quite high values of Sommerfeld's constant γ; this is a consequence of the high density of states $N(0)$ on the Fermi surface. This to a significant degree determines the high values of the critical parameters of these systems. On the other hand, for molybdenum sulfides with high values of the critical parameters (Mo_6S_8Sn and Mo_6S_8Pb) the temperature dependence of the specific heat can be represented in the form

$$C_p = \gamma T + AC_E + BC_D,$$

where C_E and C_D are the Einstein and Debye components of the specific heat of the lattice. At the same time, for molybdenum sulfides with low values of H_{c2}, such as, for example, $Mo_6S_8Cu_2$, the Einstein component of the specific heat is absent. If this correlation is valid also for other systems of this class of compounds, then it may be supposed that the high values of H_{c2} must be due to the existence of intense modes of optical oscillation in their phonon spectrum.

Study and comparison of molybdenum chalcogenides with high and with low values of the superconductivity parameters can contribute to a more detailed explanation of the reasons that lead to such high values of H_{c2} and $(\partial H_{c2}/\partial T)_{max}$. There is every reason to suppose that the parameters that have been attained in this class of superconductors are not the limiting ones. The carrying out of further investigations will probably make possible still further increase of their values.

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[2] When the specimen did not have sufficiently good thermal contact with the cryoagent, the values of H_{c2} were too low, and in the neighborhood of the λ point of liquid helium a break was observed on the H_{c2} (T) curve.[5]

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