

also is the possibility that Rauh's method of deposition produced a preferred orientation in the sample as contrasted to a polycrystalline surface. A more reasonable explanation would be based on the assumption that the lattice spacing of the body-centered cubic uranium films deposited on the body-centered cubic tungsten is smaller than that for the natural uranium metal. This would be consistent with observations made on other metals. The lattice parameter,  $a$ , for body-centered cubic uranium is

3.55 Å<sup>23</sup>; the same parameter for body-centered cubic tungsten is 3.16 Å. It therefore seems possible that Rauh's value, 3.47 eV, is the work function for clean body-centered cubic uranium with an artificially compressed lattice spacing, while the value of 3.39 eV reported here is the work function for clean, normal, body-centered cubic uranium.

<sup>23</sup> P. Chiotti, H. Klapfer, and W. White, *Am. Soc. Metals* **51**, 231, 236 (1958).

## Superconducting Critical Field of Single-Crystal Mo<sub>3</sub>Re

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Critical field measurements were performed on a cylindrical rod of single-crystal Mo<sub>3</sub>Re. The isothermal, magnetic transitions were extremely sharp and reversible, indicating that the specimen was approaching nearly ideal properties. The principal data are:  $T_c = 9.80^\circ\text{K}$ ,  $H_0 = 530$  gauss,  $(dH_c/dT)_{T=T_c} = -114$  gauss/deg. The deviation from parabolic behavior  $D(t)$  indicated a positive maximum value of 0.065. On the basis of this present work, we suggest a possible correlation between the thermodynamic critical field and the "filamentary" critical field noted for the high-field superconducting materials.

THE superconductivity of the refractory metal alloy, Mo<sub>3</sub>Re, was first reported by Hulm.<sup>1</sup> Subsequent work by Kunzler *et al.*<sup>2</sup> showed that this material could be drawn into wire suitable for fabricating superconducting solenoids. It was further shown that such wire, if cold worked as much as possible, remained superconducting in magnetic fields up to about 15 kilogauss. It is of considerable interest to inquire how this field for the destruction of supercurrents, which we suggest be called the Kunzler field  $H_K$  is related to the true thermodynamic critical field  $H_c$ . Since  $H_c$  values are not available for Mo<sub>3</sub>Re, we decided to investigate these with the aid of single crystals.

Critical field measurements were performed on a cylindrical rod of single crystal Mo<sub>3</sub>Re, 180 mm by 8 mm, prepared by electron beam melting and repeated zone refining. Magnetic induction versus magnetic field plots were taken at various temperatures using a ballistic induction technique.<sup>3</sup> Temperatures were determined above 4.2°K with a constant-volume gas thermometer<sup>4</sup> and below 4.2°K using the helium vapor pressure scale. The isothermal, magnetic transitions were extremely sharp and reversible, indicating that the specimen was approaching nearly ideal properties as is usually found only in high-purity, "soft" superconductors.

Figure 1 shows the threshold magnetic field  $H_c$  versus temperature representing the equilibrium boundary be-

tween the normal and superconducting states. The principal data are:

$$T_c = 9.80^\circ\text{K},$$

$$H_0 = 530 \text{ gauss } (T=0),$$

$$dH_c/dT = -114 \text{ gauss/deg } (T=T_c).$$

The deviation from parabolic behavior  $D(t)$  calculated from the relation

$$D(t) = (H_c/H_0) - [1 - (T/T_c)^2],$$

indicated a positive maximum value of 0.065.

The coefficient of the electronic specific heat in the normal state,  $\gamma$ , can be approximately calculated from the relation

$$V(H_0)^2/8\pi = \frac{1}{4}\gamma T_c^2, \quad (1)$$

where  $V$  is the atomic volume. Using  $V = 9.252 \text{ cm}^3/\text{mole}$  (private communication from A. Taylor), we obtain a  $\gamma$  value of 0.43 millijoules per mole deg<sup>2</sup>. This value of  $\gamma$  is close to the values for either Mo or Re, and suggests that for Mo<sub>3</sub>Re the density of states lies at a minimum in the  $d$ -band density of states versus energy curve. Possibly, in the above calculation,  $H_0$  and subsequently  $\gamma$  should be adjusted as suggested by Goodman.<sup>5</sup> Current calorimetric measurements, however, should indicate whether this correction is necessary.

In Table I, the thermodynamic, critical field value obtained for Mo<sub>3</sub>Re in the present work is compared with the Kunzler field for this material. A similar

<sup>1</sup> J. K. Hulm, *Phys. Rev.* **98**, 1539 (1955).

<sup>2</sup> J. E. Kunzler, E. Buehler, F. S. L. Hsu, B. T. Matthias, and C. Wahl, *J. Appl. Phys.* **32**, 325 (1961).

<sup>3</sup> J. K. Hulm and B. B. Goodman, *Phys. Rev.* **106**, 659 (1957).

<sup>4</sup> J. K. Hulm and R. D. Blaugher, *Cryogenics* **1**, 229 (1961).

<sup>5</sup> B. B. Goodman, *Phys. Rev. Letters* **6**, 597 (1961).

TABLE I. Bulk critical fields and Kunzler fields for "high-field" superconductors.

	$H_c(T=4.2^\circ)$	$H_K(T=4.2^\circ)$	$H_K/H_c$
$\text{Mo}_3\text{Re}$	466	15 000 <sup>b</sup>	32
$\text{Nb}+25\% \text{ Zr}$	2500 <sup>c</sup>	70 000 <sup>c</sup>	28
$\text{Nb}_3\text{Sn}$	6000 <sup>a</sup>	>200 000 <sup>d</sup>	33

<sup>a</sup> R. M. Bozorth, A. J. Williams, and D. D. Davis, Phys. Rev. Letters **5**, 148 (1960).

<sup>b</sup> J. E. Kunzler, E. Buehler, F. S. L. Hsu, B. T. Matthias, and C. Wahl, J. Appl. Phys. **32**, 325 (1961).

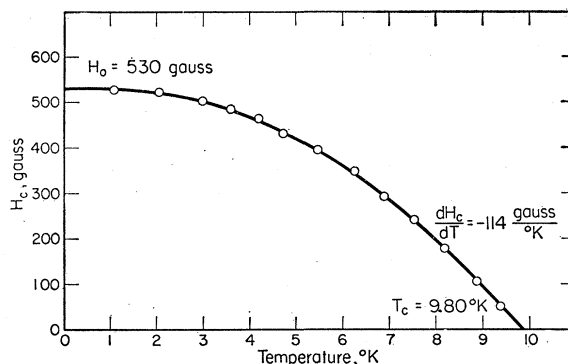
<sup>c</sup> P. R. Aron and H. C. Hitchcock (private communication, to be published).

<sup>d</sup> J. E. Kunzler (private communication).

<sup>e</sup> Estimated from measurements on a polycrystalline sample.

comparison is made utilizing approximate data for  $\text{Nb}+25\% \text{ Zr}$  and  $\text{Nb}_3\text{Sn}$ . For each of these materials,  $H_K$  is taken from the curve of critical current  $I_c$  versus applied magnetic field.  $H_K$  is defined as the field at which the plateau region of critical current ends and  $I_c$  commences its steep descent to zero. While  $H_K$  seems to depend somewhat on the physical and chemical inhomogeneities present in the material, a saturation point appears to be attained as the concentration of these inhomogeneities is increased. The  $H_K$  values in Table I are the maximum values so far reported for each material.

Apparently,  $H_K/H_c$  lies in the vicinity of 30 for the high-field superconductors which have been so far studied. This is surprising in view of the fact that the materials are of different metallurgical character and, moreover, were studied under different conditions. It

FIG. 1. Critical field vs temperature,  $\text{Mo}_3\text{Re}$ .

suggests to us that perhaps the basic mechanism of the formation of high-field, superconducting filaments or plates is the same for these three materials, at least in the bulk state.

Finally, we note that the surprisingly low Kunzler field for the transition metal alloy,  $\text{Mo}_3\text{Re}$ , stems directly from a low value of the bulk critical field. We suggest that the region between Groups 6 and 7 is not favorable for extremely high Kunzler fields, and that the molybdenum-technetium system will exhibit  $\gamma$ ,  $H_c$ , and  $H_K$  values similar to those of other high-field superconductors.

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## Nonlinear Optical Effects

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A number of possible nonlinear light effects in solids are discussed where the optical properties of a medium depend upon the value of the incident  $E$  and  $H$  radiation field; as a consequence of the nonlinear properties of these effects and their intrinsic fast response times, the possibility exists of producing harmonic generation and mixing at infrared and visible frequencies. The theory of multiple-photon excitation of an electron from the valence to the conduction in a solid is developed. It is shown that this process exhibits an intensity-dependent absorption edge at photon energies below the minimal energy gap of a solid. The experimental conditions for observing such transitions are considered; presently available optical maser sources of radiation are of sufficient intensity to enable double-quantum processes to be experimentally observable in semiconductors and insulators.

WITH the present availability of intense monochromatic sources of radiation in the visible and infrared regions of the spectrum utilizing optical masers,<sup>1-3</sup> the  $E$  and  $H$  fields that can now be incident

<sup>1</sup> T. H. Maiman, Nature **187**, 493 (1960).

<sup>2</sup> R. J. Collins, D. F. Nelson, A. L. Schawlow, W. L. Bond, C. G. B. Garrett, and W. K. Kaiser, Phys. Rev. Letters **5**, 303 (1960).

<sup>3</sup> P. P. Sorokin and M. J. Stevenson, Phys. Rev. Letters **5**, 557 (1960).

upon a substance are of sufficient intensity to allow a number of classical and quantum mechanical nonlinear optical effects to be observable. Under these conditions, the high-frequency permittivity, permeability, or conductivity of a medium can be field dependent. Maxwell's equations for the medium will no longer be linear and the principle of superposition will no longer apply, so that waves of different frequencies can interact. Quantum mechanically, a nonlinear response to an intense