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Marezio M, Dernier P D, Remeika J P, Corenzwit E & Matthias B T. Superconductivity of ternary sulfides and the structure of $PbMo_6S_8$. *Mater. Res. Bull.* 8:657-68, 1973. [Bell Laboratories, Murray Hill, NJ]

This article reported the structural data for $PbMo_6S_8$. This compound is the prototype of an extremely rich series of superconducting/ magnetic materials that exhibit remarkable low-temperature properties. [The *SCI*® indicates that this paper has been cited in more than 140 publications.]

The Ternary Molybdenum Sulfides

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During the 1960s, one of the most active groups in the search for new superconducting materials (the high T_c superconductors were science fiction then) was that headed by the late Bernd T. Matthias. In his search, Bernd developed empirical rules that were very famous, but not always in a positive way. Not everybody knew that Bernd himself did not believe them. His secret was not the rules but the fact that he knew how to put two chemical elements together. After the elements, the binaries, and the pseudobinaries, it was easy (at least a *posteriori*) to begin to look into ternary compounds. Bernd used to spend a few days a fortnight at Bell Labs and, being on San Diego time, he would come back to the laboratory after dinner and spend an hour or so in the library. One night, in January 1972, Bernd found an article in the *Journal of Solid State Chemistry*[1] that described new ternary molybdenum sulfides. He told Ernie Corenzwit to prepare these compounds by following the recipe given by the French group, and, by magnetic susceptibility measurements, we determined that the Pb and Sn compounds became superconducting with relatively sharp transitions at 13.2K and 11.3K, respectively.[2]

The structure of these compounds could only be determined by the use of single crystal data. Within a week or so, Joe Remeika was able to prepare a few crystals of the Pb compounds, though, unfortunately, they were twinned. However, we were able to determine the formula (MMo_6S_8 with M=Pb, Sn, Cu, etc.) as well as the structure. These ternary molybdenum sulfides proved to be very important compounds. For example, in 1973, ø. Fischer et al., and his collaborators at the University of Geneva (Switzerland), reported on the very high critical magnetic fields for some of the compounds having the $PbMo_6S_8$ structure.[3]

By now, Bernd had lost interest in the ternary molybdenum sulfides. In 1976, he and his Bell Labs collaborators reported the existence of superconductivity in rare-earth ternary borides, such as $RERh_4B_4$.[4] The highest T_c was 11.5K. This proved to be more than just another series because, early in 1977, Bernd and his La Jolla collaborators reported the first example of "reentrant" superconductivity.[5] This was a great discovery, as it proved the usefulness of the ternary compounds with at least three sublattices. Almost simultaneously, M. Ishikawa and Fischer[6] at Geneva reported the same type of phenomenon for $HoMo_6S_8$.

By the late 1970s, the activity on ternary superconductors was so intensive that a meeting was organized at Lake Geneva, Wisconsin, in 1980. Bernd gave the opening talk, entitled "The Enigma of Ternary Compounds," but he chose to talk about the oxide superconductor $BaPb_{.75}Bi_{.25}O_3$ (T_c=12K), discovered five years earlier by A.W. Sleight et al.[7] In retrospect, I found it strange that Bernd would be interested again in oxides because, in 1973, his La Jolla collaborators had discovered that $LiTi_2O_4$ becomes superconducting at ~11K.[8] Unfortunately, Bernd's contributions in oxides ceased four weeks later with his death on October 26, 1980.

It seems to me that with Bernd's death, except for the discovery of the heavy fermion systems, superconductivity went into a stagnant period until the great discovery of high T_c superconductors by J.G. Bednorz and K.A. Müller[9] that put us all back to work.

1. **Chevrel R, Sergent M & Prigent J.** Sur des nouvelles phases sulfurées ternaires du molybdène. *J. Solid State Chem.* 3:515-9, 1971. (Cited 220 times.)
2. **Matthias B T, Marezio M, Corenzwit E, Cooper A S & Barz H E.** High-temperature superconductors, the first ternary system. *Science* 175:1465-6, 1972. (Cited 135 times.)
3. **Odermatt R, Fischer Ø, Jones H & Bongi G.** Upper critical fields of some ternary molybdenum sulphides. *J. Phys. C—Solid State Phys.* 7:L13-5, 1974. (Cited 75 times.)
4. **Matthias B T, Corenzwit E, Vandenberg J M & Barz H.** High superconducting transition temperatures of new rare earth ternary borides. *Proc. Nat. Acad. Sci. USA* 74:1334-5, 1977. (Cited 165 times.)
5. **Fertig W A, Johnson D C, DeLong L E, McCallun R W, Maple M B & Matthias B T.** Destruction of superconductivity at the onset of long-range magnetic order in the compound $ErRh_4B_4$. *Phys. Rev. Lett.* 38:987-90, 1977. (Cited 285 times.)
6. **Ishikawa M & Fischer Ø.** Destruction of superconductivity by magnetic ordering in $Ho_{1.2}$ Mo_6S_8. *Solid State Commun.* 23:37-9, 1977. (Cited 170 times.)
7. **Sleight A W, Gillson J L & Bierstedt P E.** High temperature superconductivity in the $BaPb_{1-x}Bi_xO_3$ system. *Solid State Commun.* 17:27-8, 1975. (Cited 360 times.)
8. **Johnston D C, Parkash H, Zachariasen W H & Viswanathan R.** High temperature superconductivity in the Li-Ti-0 ternary system. *Mater. Res. Bull.* 8:777-84, 1973. (Cited 115 times.)
9. **Bednorz J G & Müller K A.** Possible high T_c superconductivity in the Ba-La-Cu-O system. *Z Phys. B—Condens. Matter* 64:189-93, 1986. (Cited 3,515 times.)

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