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Letter

Superconductivity of $SrSi_2$ and $BaGe_2$ with the α-$ThSi_2$-type structure

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Of various divalent metal disilicides MSi_2 and digermanides MGe_2 ($M \equiv$ Yb, Ca, Eu, Sr, Ba) only $EuSi_2$ crystallizes in the tetragonal α-$ThSi_2$-type structure at ambient pressure [1]. The characteristic feature of this structure is a three-dimensional net built up of three-connected metalloid atoms. The repeat unit of four atoms is planar [2]. However, in this class of materials three additional phases with the α-$ThSi_2$-type structure are obtained when the MSi_2 and MGe_2 compounds are heated under pressure and are then quenched to ambient conditions. From X-ray powder investigations this structure was identified for the high pressure–high temperature (HPHT) polymorph of $CaSi_2$ [3, 4] and more recently, in a systematic study on these compounds, also for that of $SrSi_2$ [5] and $BaGe_2$ [6].

Up to now in these MSi_2 and MGe_2 compounds superconductivity has been observed only for the α-$ThSi_2$-type phases of $CaSi_2$ and defect $SrSi_{2-x}$ ($x = 0.5$) [4]. $EuSi_2$ orders antiferromagnetically at 40 K [7] and is therefore not expected to become superconducting at lower temperatures. The purpose of this work was to search for possible superconductivity in stoichiometric $SrSi_2$ and $BaGe_2$ with the α-$ThSi_2$-type structure.

High purity samples of $SrSi_2$ and $BaGe_2$ were prepared by direct synthesis of electronic grade silicon or germanium respectively with ultrahigh-vacuum-distilled strontium or barium [8] in an inductively heated copper boat. Evaporation losses were determined in preliminary experiments. Ambient pressure phases were transformed by HPHT treatment in a belt-type apparatus [9]. Typical conditions were 40 kbar and 1000 °C for 15 min and subsequent quenching to ambient conditions.

The superconducting transition temperatures T_c were measured inductively using a standard low frequency mutual inductance bridge. We also checked the depression of the critical temperatures with increasing magnetic field.

TABLE 1

Superconducting transition temperatures T_c

Composition	T_c (K)
$CaSi_2$	1.37 ± 0.02
$CaSi_{1.9}$	1.35 ± 0.04
$CaSi_{2.2}$	1.37 ± 0.02
$SrSi_2$	3.1 ± 0.3
$BaGe_2$	4.93 ± 0.1

In Table 1 we show our values of T_c for $CaSi_2$, $SrSi_2$ and $BaGe_2$. In the case of $CaSi_2$ our value is roughly 0.2 K lower than that reported previously [4]. For this reason we also measured T_c for off-stoichiometric samples but found very little influence of the silicon content on the transition temperature (see Table 1). A change of the ratio Ca:Si in the range up to about 10% also left the lattice parameter virtually unaffected; it remained constant within the experimental uncertainty. It may therefore be assumed that the α-$ThSi_2$-type structure is stable for stoichiometric $CaSi_2$ only. A reasonable explanation of the somewhat higher value of T_c obtained earlier for $CaSi_2$ cannot therefore be based on differences in stoichiometry but rather on a possible small content of strontium in the samples used in the former investigations. Commercially available calcium often contains more than 1% Sr impurity. In solid solutions $Ca_{1-x}Sr_xSi_2$ an increase of T_c above the value for pure $CaSi_2$ may be expected even for small x since T_c for $SrSi_2$ is more than twice as high as that of $CaSi_2$. It is interesting to note that $BaGe_2$, which in its ambient pressure phase is a semiconductor, has the highest value for T_c, above the values for $CaSi_2$ and $SrSi_2$ which in their ambient pressure phases are semimetals.

Unfortunately no clear evidence for a dependence of T_c on the atomic number of the metal atoms can be established for the silicon series. In our pressure and temperature range (45 kbar and 1500 °C) $BaSi_2$ does not form in the α-$ThSi_2$-type structure. Two other HPHT modifications are obtained instead, namely the $SrSi_2$- and $EuGe_2$-type structures. The same is true for the digermanides since in dimorphic $SrGe_2$ other structure types than that of α-$ThSi_2$ are found. However, this particular structure can be prepared in a limited range of solid solutions of $BaGe_{2-x}Si_x$ and $Ba_{1-x}Sr_xGe_2$. Investigations of these compounds may show the tendency of increasing T_c with increasing radius of the metal atoms, as is indicated by our measurements.

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