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The AlB_2 Structure in the EuM_xSi_{2-x} System

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The AlB_2 type hexagonal structure was studied in the EuM_xSi_{1-x} system, for M = Fe, Co, Ni, Cu, Ag and Au. Only $EuCu_{0.5}Si_{1.5}$ and $EuAg_{0.67}Si_{1.33}$ crystallize as single phases. The Mössbauer spectrum of $EuCu_{0.5}Si_{1.5}$ shows europium to be divalent. Valence electron concentration and packing of the layers in the $LnCu_xSi_{2-x}$ and $LnAg_xSi_{2-x}$ systems is discussed. Higher stability of the $EuCu_xSi_{2-x}$ and $EuAg_xSi_{2-x}$ compounds is explained by the close similarity in size of Cu and Ag to Si.

Ternary rare earth silicides crystallizing in the AlB_2-type hexagonal structure, have been reported previously (*1–3*). The AlB_2 type structure is built up from layers of the nonmetals with the metals interspersed. In the ternary rare earth silicides part of the silicon in the hexagon-like layers is replaced by transition metals. The close packing in the ternary compounds depends on the penetration of the rare earth atoms into the silicon layers.

The present work deals with compounds of the EuM_xSi_{2-x} system (M = Fe, Co, Ni, Cu, Ag and Au) having the AlB_2 type hexagonal structure. Some of the compounds were first observed as second phases in our studies of the $ThCr_2Si_2$ type silicides (*4*, *5*); these have now been prepared as single phases.

Experimental

The compounds were prepared by melting together europium, the transition metals and silicon (all of 99.9% purity) in alumina crucibles in an induction furnace under a protective atmosphere of argon. They were X-ray analyzed by a Philips Diffractometer using Ni-filtered Cu*Kα* radiation. Mössbauer effect measurement has been carried out using 22 keV γ rays of ^{151}Eu isotope. The γ rays were obtained from a ^{151}Sm source in the form of Sm_2O_3.

Results and Discussion

In Table I, cell dimensions of the AlB_2 type EuM_xSi_{2-x} compounds are listed. The AlB_2 type structure was not observed in the $EuFe_xSi_{2-x}$ system. $EuCu_{0.5}Si_{1.5}$ and $EuAg_{0.67}Si_{1.33}$ crystallize as pure AlB_2-type phases, but when the metal content was increased, the $ThCr_2Si_2$-type structure appeared as a second phase. None of the Co, Ni, and Au compounds could be obtained as single phases.

In Fig. 1 the Mössbauer spectrum of Eu in $EuCu_{0.5}Si_{1.5}$ is shown. The isomer shift found relative to Eu_2O_3 is -11 ± 0.2 mm/sec, which is the isomer shift found for divalent europium in metallic compounds (*6*).

In Table II lattice constants of $EuCu_{0.5}Si_{1.5}$

TABLE I

LATTICE CONSTANTS OF HEXAGONAL AlB_2-TYPE EuM_xSi_{2-x} COMPOUNDS

	a (Å)	*c* (Å)
$EuCo_{0.5}Si_{1.5}$	4.046	4.500
$EuNi_{0.5}Si_{1.5}$	4.034	4.496
$EuCu_{0.5}Si_{1.5}$	4.080	4.466
$EuAg_{0.67}Si_{1.33}$	4.203	4.465
$EuAu_{0.5}Si_{1.5}$	4.150	4.515

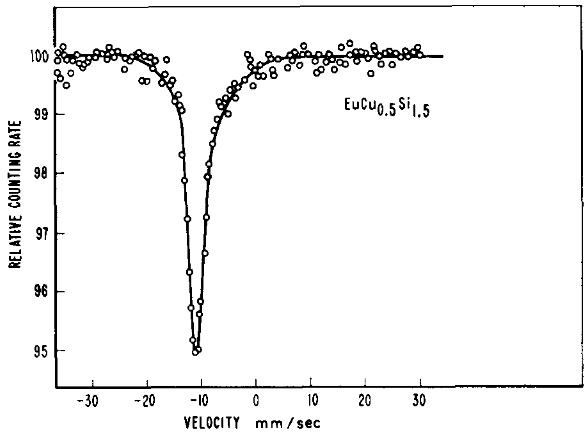

FIG. 1. Mössbauer spectrum of Eu in $EuCu_{0.5}Si_{1.5}$.

and $EuAg_{0.67}Si_{1.33}$ are compared with the lattice parameters of the corresponding compounds of the other rare earth metals. This comparison shows significant increase in c of the Eu-compounds, while a changes less sha-ply. Assuming that europium is divalent in the AlB_2 type EuM_xSi_{2-x} compounds, as is found for $EuCu_{0.5}Si_{1.5}$, the valence electron concentration in the Eu-compounds is decreasing and consequently the bonds in the graphitic layers will become weaker. The AlB_2 structure forms therefore at lower Ag content than in the case of the other relatively big rare earth metals (*3*). The effective space in the hexagons is, however, still small for efficient penetration of the relatively large europium atoms. The packing between the metallic and nonmetallic layers will be therefore less dense and c, which represents the distance between the layers of the Eu atoms, must increase.

TABLE II

LATTICE CONSTANTS AND VALENCE ELECTRON CONCENTRATION (VEC) OF HEXAGONAL (*P6/mmm*) AlB_2-TYPE $LnCu_xSi_{2-x}$ AND $LnAg_xSi_{2-x}$ COMPOUNDS

	a (Å)	c (Å)	*vec*
$EuCu_{0.5}Si_{1.5}$	4.080	4.496	2.833
$LaCu_{0.5}Si_{1.5}$[a]	4.144	4.286	3.166
$CeCu_{0.5}Si_{1.5}$[a]	4.136	4.237	3.166
$EuAg_{0.67}Si_{1.33}$	4.203	4.465	2.666
$DyAg_{0.67}Si_{1.33}$	4.133	4.036	3.000
$ErAg_{0.67}Si_{1.33}$	4.196	4.095	3.000

[a] From Ref. (*1*).

The mean radii of the nonmetals in the AlB_2 structure and the transition metals substituting part of them, equals to a good approximation to $a/\sqrt{3}$. The size of the transition metals in the different EuM_xSi_{2-x} compounds will be in the order of these mean radii, namely $Co < Ni < Cu < Si < Ag < Au$. The radii of Cu and Ag are closest to that of Si, hence these atoms form most easily AlB_2 type compounds. In the case of Co, Ni and Au the AlB_2 type phase appears with additional phases.

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