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Structure Field Maps for Sulfides of Composition AB_2X_4

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Structure field maps for ternary sulfides crystallizing in common AB_2X_4 structures are given. They have been obtained from a plot of mean values of pseudopotential radii. There is a good separation of the fields for the different structures. The maps are used to predict possible compositions for new quaternary compounds of $ZnIn_2S_4$ type.

Introduction

For some years we have been involved in the preparation of new compounds crystallizing in one of the various polytypes of $ZnIn_2S_4$. Using a concept based on simple ideas of site preference energy (*1*) many new materials with one of these structures have been prepared. But there are some examples where this concept failed, for instance, in the case of the systems MGa$_2$S$_4$–MCr$_2$S$_4$ with M = Zn, Cd, and Hg, where no compounds with $ZnIn_2S_4$ structure are formed (*2*). We researched structure field maps to obtain a basis for these findings, but the literature we found did not contain the $ZnIn_2S_4$-type structures and thus could not provide any answers. Therefore, we started to work out a new map especially for the structure types involved in the systems we were investigating.

The latest and most promising development for the preparation of structure field maps is the use of pseudopotential radii as coordinates of the plot. Using such radii Zunger (*3*) was able to draw maps for *AB* compounds in which the fields for the different structures were well separated and Burdett *et al.* (*4*) could separate normal and inverse spinels. So we decided to make a structure field map based on pseudopotential radii.

Structure Field Maps

The theory for the calculation of pseudopotential radii is given in the papers by Zunger (*3*) and Bloch and Schatteman (*5*) and the references therein. Roughly speaking, the radii are calculated taking into account the influence of a core potential on electrons with different orbital quantum numbers. So for a single element, different orbital radii r_l (l = 1, 2, 3), i.e., r_s, r_p, and r_d, are obtained. Values of these radii for 70 elements are given by Zunger (*3*). Similar values can also be found in the paper by Bloch and Schatteman (*5*), but we used the more complete table from Zunger.

For the construction of structural maps for *AB* compounds Zunger used the following combinations of the radii r_s and r_p:

$$R_\sigma^{AB} = |(r_s^A + r_p^A) - (r_s^B + r_p^B)|$$

$$R_\pi^{AB} = |r_s^A - r_p^A| + |r_s^B - r_p^B|.$$

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According to Zunger, R_σ^{AB} is a measure of the difference between the total effective core radii of atoms A and B, and R_π^{AB} measures the sum of the orbital nonlocality of the s and p electrons on each atom. According to Bloch and Schatteman (*5*), who use similar coordinates, R_π^{AB} measures the average propensity of the two atoms for s–p hybridization (for small values of R_π^{AB} tetrahedral coordination is preferred).

These coordinates cannot be used directly for the preparation of a two-dimensional structural separation plot for ternary compounds because in this case four independent coordinates (R_σ^{AX}, R_π^{AX}, R_σ^{BX}, R_π^{BX}) exist. One possibility in using pseudopotential radii in making out a planar structural map for ternary compounds is followed by Burdett *et al.* (*4*). They apply $R_\sigma^A = r_s^A + r_p^A$ and $R_\sigma^B = r_s^B + r_p^B$ as coordinates for the separation of normal and inverse spinels, where A and B are the two different cations according to the composition AB_2X_4. Such maps, which are valid only for compounds with the same anion X, are equivalent to those based on effective ionic radii given for instance by Muller and Roy (*6*). We extended this type of map to other structures which occur among ternary sulfides AB_2S_4 (see Fig. 1). Since one can find pseudopotential radii only for lanthanum but not for the lanthanoides, only few examples of the Th_3P_4 type are given in the map. For the same reason, compounds with MnY_2S_4, Yb_3S_4, and $CaFe_2O_4$ structure are not included in the map.

Figure 1 shows a good separation of the β-K_2SO_4-, Th_3P_4-, and olivine-structure fields, but spinel and Cr_3S_4 as well as thiogallate and $ZnIn_2S_4$ are not resolved. Thus, a map based on the effective core radii of the cations only cannot be used to solve the question why no compound with $ZnIn_2S_4$ structure is formed in the case of the systems MGa$_2$S$_4$–MCr$_2$S$_4$ with M = Zn, Cd, or Hg.

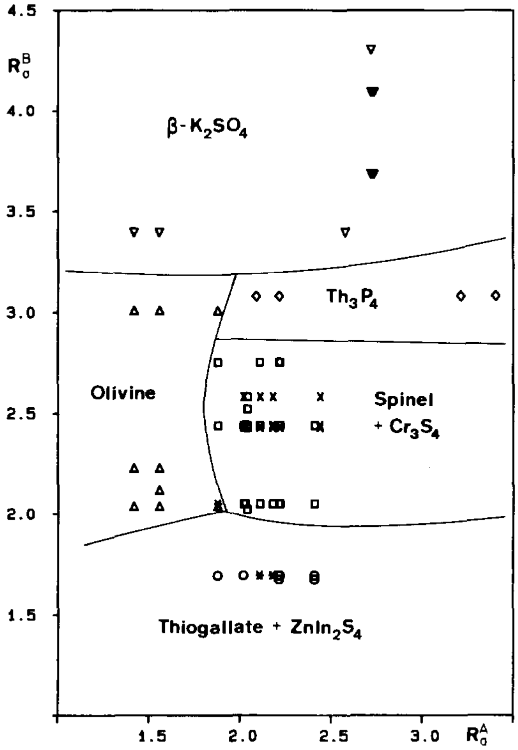

FIG. 1. Structural separation plot for ternary sulfides AB_2S_4 using R_σ^A and R_σ^B as coordinates. ▽, β-K_2SO_4 type; △, olivine type; ◇, Th_3P_4 type; □, spinel type; ×, Cr_3S_4 type; ○, thiogallate type; *, $ZnIn_2S_4$ type.

We therefore tried to make out another map based on different coordinates. For this purpose we used the mean values of the Zunger coordinates R_σ and R_π,

$$\overline{R}_\sigma = (xR_\sigma^{AS} + yR_\sigma^{BS})/(x + y)$$

$$\overline{R}_\pi = (xR_\pi^{AS} + yR_\pi^{BS})/(x + y),$$

where x and y are the stoichiometric factors for A and B, respectively. This method for the computation of the coordinates has the advantage that it can easily be expanded to quaternary compounds. A structure separation plot based on these coordinates can be considered as a projection of the structural areas on a section through the four-dimensional space spanned by the coordinates

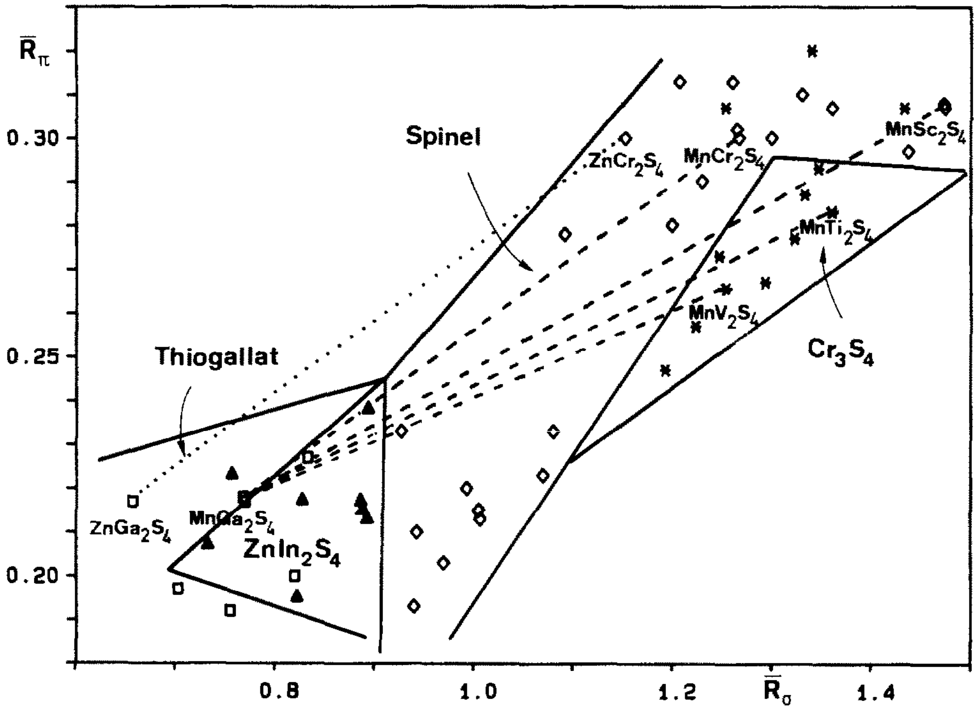

FIG. 2. Structural separation plot for ternary sulfides AB_2S_4 using mean values of R^{AX} and R^{BX} as coordinates. ◇, spinel type; *, Cr_3S_4 type; □, thiogallate type; ▲, $ZnIn_2S_4$ type. ---, systems in which new layered materials should be found; ... , no compound with layered structure has been found in this system.

R_σ^{AX}, R_π^{AX}, R_σ^{BX}, and R_π^{BX}. Projections on different planes should give similar results.

The map shown in Fig. 2 concentrates on four main structure types occurring among AB_2S_4-type compounds. A list of the compounds and their values of $\bar{R}_\sigma$ and $\bar{R}_\pi$ is given in Table I. The separation between the different structures is good, even for the $ZnIn_2S_4$ type. Only a few compounds are misplaced: these are the Cr_3S_4-type compounds Cr_3S_4, $CrTi_2S_4$, and $NiCr_2S_4$ which are found in the spinel field, and the thiogallate $HgAl_2S_4$ which is located in the $ZnIn_2S_4$ area. Two features of this plot are remarkable: (i) the structure fields form a relatively small band which is located diagonally in the plot, i.e., there are no compounds with high values of $\bar{R}_\sigma$ and small values of $\bar{R}_\pi$ and vice versa. (ii) There is also a huge area in the spinel field which is empty. In this region we would expect to find compounds of the type MMn_2S_4 with trivalent manganese, for instance, $ZnMn_2S_4$.

Looking at this map one can find reasons for our former finding that in the system $ZnGa_2S_4$–$ZnCr_2S_4$ no compound with a layer structure is formed: all quaternary compounds $ZnGa_xCr_{2-x}S_4$ would lie on the connecting line (this is the dotted line in Fig. 2) between the two ternary compounds. This line does not intersect the $ZnIn_2S_4$ field due to the relatively high value for $\bar{R}_\pi$, i.e., the low mean propensity for s–p hybridization. The two border compounds $ZnCr_2S_4$ and $ZnGa_2S_4$ have higher stability than a mixed composition. The same arguments hold for the analogous sys-

TABLE I

COMPOUNDS INCLUDED IN THE STRUCTURAL SEPARATION PLOT

Cr_3S_4 type			Thiogallate type			$ZnIn_2S_4$ type		
	$\bar{R}_\sigma$	$\bar{R}_\pi$		$\bar{R}_\sigma$	$\bar{R}_\pi$		$\bar{R}_\sigma$	$\bar{R}_\pi$
$CrTi_2S_4$	1.43	0.31	$CdAl_2S_4$	0.75	0.19	$ZnIn_2S_4$	0.89	0.21
$FeTi_2S_4$	1.32	0.28	$HgAl_2S_4$	0.82	0.20	$FeGa_2S_4$	0.73	0.21
$CoTi_2S_4$	1.29	0.27	$ZnGa_2S_4$	0.66	0.22	$NiGa_2S_4$	0.76	0.22
$NiTi_2S_4$	1.35	0.29	$CdGa_2S_4$	0.77	0.22	$CdGaInS_4$	0.89	0.22
CrV_2S_4	1.33	0.29	$HgGa_2S_4$	0.83	0.23	$MnGaInS_4$	0.89	0.21
FeV_2S_4	1.22	0.26	$CoGa_2S_4$	0.70	0.20	$CoGaInS_4$	0.82	0.19
CoV_2S_4	1.19	0.25	$MnGa_2S_4$	0.77	0.22	$MnGa_{1.7}Cr_{0.3}S_4$	0.89	0.24
NiV_2S_4	1.25	0.27				$CoGa_{1.7}Cr_{0.3}S_4$	0.83	0.22
Cr_3S_4	1.34	0.32						
			Spinel type					
	$\bar{R}_\sigma$	$\bar{R}_\pi$		$\bar{R}_\sigma$	$\bar{R}_\pi$		$\bar{R}_\sigma$	$\bar{R}_\pi$
$MgIn_2S_4$	0.94	0.21	$CdIn_2S_4$	1.00	0.21	$HgIn_2S_4$	1.07	0.22
$FeIn_2S_4$	0.97	0.20	$CoIn_2S_4$	0.94	0.19	$NiIn_2S_4$	0.99	0.22
$MnIn_2S_4$	1.01	0.21	$CrIn_2S_4$	1.08	0.23	CuV_2S_4	1.20	0.28
$CuTi_2S_4$	1.30	0.30	$CuCo_2S_4$	0.93	0.23	$CuRh_2S_4$	1.26	0.31
$CuCr_2S_4$	1.21	0.31	$ZnCr_2S_4$	1.15	0.30	$CdCr_2S_4$	1.26	0.30
$HgCr_2S_4$	1.33	0.31	$MnCr_2S_4$	1.27	0.30	$FeCr_2S_4$	1.23	0.29
$CoCr_2S_4$	1.20	0.28	$ZnSc_2S_4$	1.36	0.31	$CdSc_2S_4$	1.47	0.31
$MnSc_2S_4$	1.47	0.31	$FeSc_2S_4$	1.44	0.30			

tems with Cd and Hg, where the situation is similar but not as evident. Both compounds $CdGa_2S_4$ and $HgGa_2S_4$ lie near the borderline between the $ZnIn_2S_4$ and the thiogallate fields. The connection lines to the corresponding chromium spinels are nearly parallel to the borderline and therefore do not intersect the $ZnIn_2S_4$ field.

The map may also be helpful in predicting new quaternary compounds with $ZnIn_2S_4$-type structures. So we are searching for new layered materials of this type in all those systems where the connection line between the two ternary compounds (they may not even exist) goes through the $ZnIn_2S_4$ field. This is shown, for example, in Fig. 2 by the dashed lines originating from $MnGa_2S_4$. First results of investigations in the systems $MnGa_2S_4$–$MnSc_2S_4$, $MnGa_2S_4$–MnV_2S_4, and $MnGa_2S_4$–$MnTi_2S_4$ show, that in each case, compounds with $ZnIn_2S_4$-type structure are formed (*7*).

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