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# Mooser–Pearson phases among the BaAl<sub>4</sub>-type derivatives

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(28. VIII. 1984)

In honor of Emanuel Mooser's 60th birthday

*Abstract.* The Mooser–Pearson rule, which defines a necessary bond condition for a solid to be nonmetallic, is applied to compounds which crystallize in the ThCr<sub>2</sub>Si<sub>2</sub> structure or in one of its variants. It appears that metallic properties are favored in the tetrelides and in the pnictides. In many cases a structure type which excludes nonmetallic properties is preferred to the type which would allow semiconductivity.

## Introduction

In the early fifties it was common among physicists to explain the occurrence of nonmetallic properties of a binary or ternary compound with Brillouin-zone calculations. The construction of the filled zone, the Jones zone, however, was a laborious task. In 1956 Mooser and Pearson published their first papers on the chemical bond in semiconductors [1]. This was a chemical approach to the problem of the conductivity character, based mainly on Pauling's valence bond theory. The crucial point here was not the long-range periodicity of the crystal lattice but the short-range bonding which is decisive also in amorphous materials. In band theory the valence electrons are treated as a collective belonging to the whole crystal. In nonmetallic solids it is a useful approximation to consider the bonding valence electrons as localized either between cation and anion in covalent crystals or on the anions in purely ionic crystals. Since the electron balance is not influenced by the degree of covalency of the bonds we can formally treat all cation–anion bonds as if they were ionic.

## The Mooser–Pearson rule

Mooser and Pearson assumed semiconductivity to be the result of the presence of predominantly covalent two-electron  $\sigma$ -bonds. This leads, through the process of electron sharing, to completely filled s and p orbitals in the valence shells of the anions. For compounds, which contain cation–anion bonds only, i.e. for normal valence compounds, this statement is equivalent to the trivial equation

$$\frac{n_c + n_a}{N_a} = 8,$$

where  $n_c$ ,  $n_a$  are the numbers of cation and anion valence electrons, respectively, and  $N_a$  is the number of anions, all per unit cell or per formula unit. Localized bonds may also occur between anions, thus reducing the number of valence electrons required from the cations:

$$\frac{n_c + n_a}{N_a} = 8 - b_a,$$

where  $b_a$  indicates the number of anion–anion bonds per anion. This is the original Mooser–Pearson condition for semiconductivity. It was soon recognized that in certain cases, like GaS, InS, GeAs, localized cation–cation bonds may form as well, so that the complete formula [2] is

$$\frac{n_c + n_a - N_c b_c}{N_a} = 8 - b_a.$$

The Mooser–Pearson criterion for nonmetallic bonding looks very simple but its application may be tricky as soon as the coordination number is no longer clearly defined [3]. In fact, many crystal structures allow a continuous transition from nonmetallic to semimetallic and metallic properties, as for example the arsenic structure in  $\text{Sb}_x\text{Bi}_{1-x}$  and the pyrite structure in  $\text{NiS}_{2-x}\text{Se}_x$ . Thus, for polycompounds, the structures of which necessarily contain at least one free site parameter, it is not a priori evident whether the anion–anion distances correspond to the single bonds required for bond saturation. In order to decide this question one needs above all a reliable structure determination.

It is easy to transform the Mooser–Pearson formula into a chemical equivalent. The valence  $\gamma$  of the cation is nothing but its number of bonding valence electrons while the anion valence  $\alpha$  is equal to  $8 - n_a/N_a$ . Thus, for a compound of composition  $\text{M}_m^{(\gamma)}\text{X}_x^{(\alpha)}$  we have (per formula unit):

$$N_c = m, N_a = x, n_c = \gamma m, n_a = 8x - \alpha x, \text{ and as a consequence}$$

$$m(\gamma - b_c) = x(\alpha - b_a),$$

which is a generalized neutrality condition. Here only the heteropolar part has to be considered:  $\gamma' = \gamma - b_c$  and  $\alpha' = \alpha - b_a$ . Or turned the other way: The valence electrons not engaged in the cation–anion bonding have to be localized in covalent M–M or X–X bonds. In the Mooser–Pearson approach these additional bonds were single bonds only, in order to keep the problem tractable. In compounds containing clusters of six or more metal atoms, for example, we have to drop this condition. But then we are lost without further knowledge (either experimental or from energy-band calculations) about the electronic configuration of the cluster. Clusters are formed mainly with 4d and 5d transition elements but also with boron.

In ordinary nonmetallic transition-element compounds the excess *d*-electrons (i.e. those not used for the chemical bonds) have to be localized on the cation and the magnetic properties must reflect the nonmetallic *d*-electron configuration. Although transition-element compounds are more problematic as far as the prediction of the conductivity character is concerned, the possibility to induce a gradual semiconductor-to-metal transition and a continuous increase of the free carriers by means of chemical substitutions renders them attractive for the study of properties which depend upon the concentration of the current carriers.

## The $\text{BaAl}_4$ structure and its derivatives

We chose to look at the  $\text{BaAl}_4$ -type family because this rather simple structure is adopted by hundreds of compounds and the number of the known representatives is still increasing. A geometrical analysis of this structure type has recently been published by Pearson and Villars [4]. The binary archetype is met in aluminides, gallides and indides of alkali and alkaline-earth metals, as well as in  $\text{ThZn}_4$ , which are all true metallic phases.

The  $\text{BaAl}_4$  structure, depicted in Fig. 1, is body-centered tetragonal (space group  $I4/mmm$ , Nr. 139) with

M in  $2(a): 0, 0, 0$

X(1) in  $4(d): 0, 1/2, 1/4; 1/2, 0, 1/4$

X(2) in  $4(e): \pm(0, 0, z)$

The large electropositive atom M is at the center of a complicated polyhedron which is a kind of truncated square prism. The X(2) atoms define a square prism with base  $a$  and height  $(1 - 2z)c$  while the X(1) atoms form an elongated square prism with base  $a/\sqrt{2}$  and height  $c/2$ . The distance  $\text{M}-8\text{X}(2)$  is usually smaller than  $\text{M}-8\text{X}(1)$ , but the difference can be rather small. The X(1) atoms in  $4(d)$

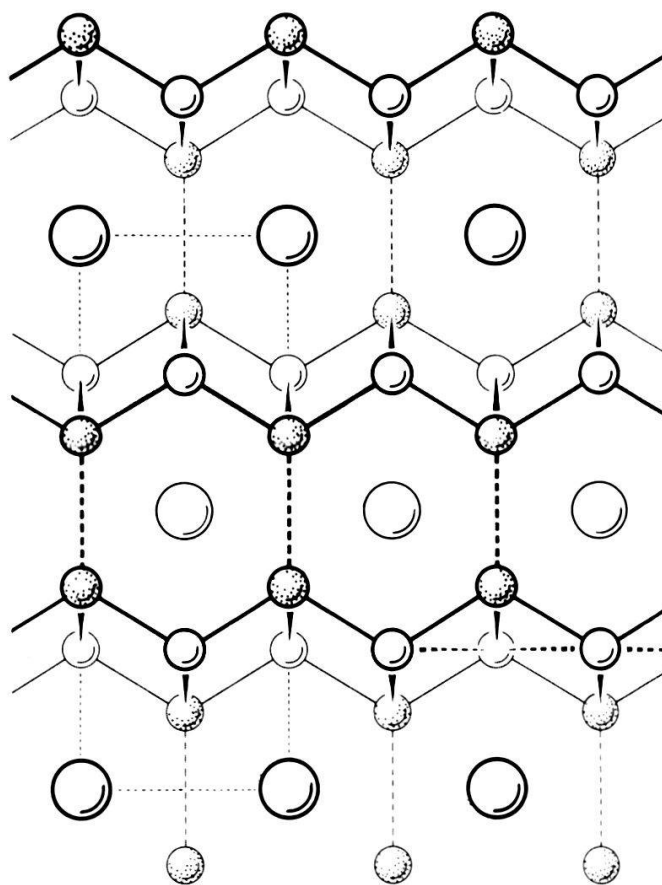


Figure 1

The  $\text{BaAl}_4$  or  $\text{ThCr}_2\text{Si}_2$  ( $\text{MT}_2\text{X}_2$ ) structure projected onto the  $(a, c)$  plane. Faint and heavy circles: atoms at  $b = 0$  and  $b = \frac{1}{2}$ , respectively. Large circles: Ba or Th (M), small open circles: Al(1) or Cr (T), small stippled circles: Al(2) or Si (X). The unit cell is indicated by dotted contours. The broken bond lines may or may not represent true bonds. M-X bonds and possible M-T bonds are not shown.

Table 1  
Occupation of the crystallographic sites in  $BaAl_4$ -related structure types.

Site	$BaAl_4$	$ThCr_2Si_2$	$La_2O_2Te$	$MoSi_2$	$ThH_2$	$TlAgTe_2^*$
2(a)	Ba	Th	Te	Mo	Th	Tl
4(d)	Al(1)	Cr	O	—	H	(Ag□)*
4(e)	Al(2)	Si	La	Si	—	Te

\*) Ordered defective type, space group  $I\bar{4}m2$  (Tl in 2(a): 0, 0, 0; Ag in 2(c): 0, 1/2, 1/4; Te in 4(e):  $\pm(0, 0, z)$ )

have four equidistant X(2) neighbors which would define an ideal tetrahedron if

$$z = \frac{1}{4} + \frac{1}{2\sqrt{2}} \frac{1}{(c/a)} \quad (\text{if } z = 3/8, \text{ then } c/a = 2\sqrt{2} = 2.83).$$

The four M neighbors define an elongated tetrahedron since  $c/a > \sqrt{2}$  in all known representatives.

The X(2) atoms are surrounded by 4X(1) + 1X(2) in square-pyramidal coordination. The M neighbors form a square pyramid with opposite orientation. Which one of these distances will represent a chemical bond critically depends upon the values of  $z$  and  $c/a$ , and these also determine the layer character.

Since Al in  $BaAl_4$  occupies two crystallographically inequivalent sites one ordered ternary variant can be formed within the same space group. All other ordered substitutions will lower the symmetry. The first possibility is realized in the  $ThCr_2Si_2$  type and its antitype, the  $La_2O_2Te$  structure. Table 1 shows the occupation of the crystallographic sites in  $BaAl_4$ -related structures. A similar variation in coordination and bonding as in the  $BaAl_4$  group is met also in the branches which are isopuntal with  $MoSi_2:CaC_2$ ,  $Cr_2Al$  and  $\beta\text{-PdBi}_2$ . A less defective ordered variant of the  $BaAl_4$  structure is found in  $Tl(Ag\Box)Te_2$  [5], claimed also for  $TlFeS_2$  ( $=TlFe_{2-x}S_2?$ ).<sup>1)</sup>

The  $La_2O_2Te$  structure type was recognized in oxyhalides  $(M_{1/2}Bi_{3/2})O_2X$  with  $M = Li, Na$ ;  $X = Cl, Br, I$ ;  $(BaBi)O_2X$  with  $X = Cl, Br$ ;  $(CdBi)O_2I$  and  $(PbSb)O_2Cl$  already in 1939 by Sillén [7]. In the structure of these compounds, however, the 4(e) position has to be occupied statistically by two different cations. A symmetry reduction (and possibly a distortion) is resulting if we replace the element in the 2(a) position by a complex like  $MoO_4$ ,  $CO_3$ ,  $[Se_{1/2}(Se_2)_{1/2}]$  or  $AsS_{5/2}$  as met in  $La_2MoO_6$ ,  $La_2O_2CO_3$ ,  $La_4O_4Se_3$  and  $La_4O_4As_2S_5$ , respectively.

These layer-type phases are reminiscent of  $BiOCl$  (or  $PbFCl$ ). In fact, a whole group of phases, called the Sillén phases, is built up of  $PbO$ -type square layers of the type  $[OPb_{4/4}]_\infty$  intercalated by halogen layers, two in the case of the  $PbFCl$  or  $BiOCl$  structure, one in the case of  $(BaBi)O_2Cl$  (where subsequent tetrahedron layers are shifted by  $(\frac{1}{2}, \frac{1}{2}, 0)$ ), and a mixture of both in the case of  $SrBi_3O_4Cl_3$  [8]. Nonmetallic properties are beyond doubt in the Sillén phases as well as in the normal valence compounds  $Ln^{3+}O_2Te$ ,  $Bi_2O_2Se$ ,  $Th_2N_2Te$ ,  $Th_2(NO)Sb$  and possible in  $U_2N_2Te$ . The M-M distances along the tetragonal axis  $(1-2z)c$  are large enough to exclude any dangerous interactions.

In  $Ce_2N_2Sb$ ,  $Ce_2O_2Sb$ ,  $Ce_2O_2Bi$ ,  $Th_2N_2Sb$ ,  $Th_2N_2Bi$ ,  $U_2N_2Sb$ ,  $U_2N_2Bi$ ,

<sup>1)</sup> For references on crystal data not given explicitly see [6].



$\text{Am}_2\text{O}_2\text{Bi}$ ,  $\text{Cm}_2\text{O}_2\text{Sb}$  and  $\text{Cm}_2\text{O}_2\text{Bi}$ , on the other hand, the cations should be half tetravalent and half trivalent, since no localized M–M or X–X bonds can shift the electron balance. Therefore metallic properties are to be expected.

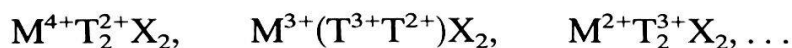
Let us turn now to the true  $\text{BaAl}_4$  derivatives. The ten possible ordered structures for ternary derivatives with the same unit cell have been described by Parthé et al. [9]. Only three of them have been observed yet: the  $\text{ThCr}_2\text{Si}_2$  [10] or  $\text{CeAl}_2\text{Ga}_2$  type [11], the  $\text{CaBe}_2\text{Ge}_2$  type [12] and the  $\text{BaNiSn}_3$  type [13]. We restrict our considerations to the 1:2:2 stoichiometry. The mirror plane through the M layers in the  $\text{ThCr}_2\text{Si}_2$  structure is lost in the  $\text{CaBe}_2\text{Ge}_2$  structure. One of the two anti-PbO-type square-layer sandwiches X–T<sub>2</sub>–X (the  $[\text{TX}_{4/4}]_\infty$  tetrahedron layers) is reversed into a PbO-type sandwich, i.e. M and X are interchanged in the upper part of the cell. There are no more X–X contacts except possibly those in the X square layer with distances  $\text{X–4X} = a/\sqrt{2}$  which would induce metallic conductivity. These square layers could also spoil a nonmetallic character in both  $\text{ThCr}_2\text{Si}_2$ - and  $\text{CaBe}_2\text{Ge}_2$ -type compounds due to T–T contacts.

A superposition of the  $\text{ThCr}_2\text{Si}_2$  and the  $\text{CaBe}_2\text{Ge}_2$  structure is met in the  $\text{BaMg}_2\text{Sn}_2$  structure [14] which therefore has a unit cell twice as high ( $b_a \leq \frac{1}{2}$ ). A structure with a unit cell half as high is offered by  $\text{CeMg}_2\text{Si}_2$  [15]. Although certain coordinations are changed the X–X pairs along the tetragonal axis still are possible.

Provided that  $c/a$  is large and  $z < 3/8$  no X–X bonds form in the  $\text{ThCr}_2\text{Si}_2$  structure. Thus normal valence bonds are possible if the distances T–4T and M–8T are large enough. In the  $\text{CaBe}_2\text{Ge}_2$  variant the distances within the square layers may be critical for either T or X atoms since  $\text{T–4T} = \text{X–4X} = a/\sqrt{2}$ .

Formally the neutrality condition would be fulfilled in the following compositions ( $b_a = 0$ ):

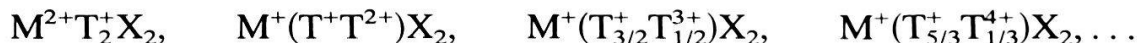
tetrelides (X = Si, Ge, Sn, Pb)



pnictides (X = P, As, Sb, Bi)



chalcogenides (X = S, Se, Te)



with  $\text{M}^{4+} = \text{Th}, (\text{U}), \text{Zr}, \text{Hf}$ ;  $\text{M}^{3+} = \text{Ln}^{3+}, \text{Bi}$ ;  $\text{M}^{2+} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Eu}, \text{Yb}, \text{Pb}$ ;  $\text{M}^+ = \text{Tl}, \text{Cs}, \text{Rb}$ ; and  $\text{T}^{4+} = \text{Si}, \text{Ge}, \text{Sn}$ ;  $\text{T}^{3+} = \text{Al}, \text{Ga}, \text{Sc}, \text{Fe}, \dots$ ;  $\text{T}^{2+} = \text{Zn}, \text{Cd}, \text{Mg}, \text{Mn}, \dots$ ;  $\text{T}^+ = \text{Cu}, \text{Ag}, \text{Li}, \dots$

An ordered defect  $\text{ThCr}_2\text{Si}_2$  variant, e.g. the  $\text{Tl}(\text{Ag}\square)\text{Te}_2$  structure, is possible in pnictides  $\text{M}^{2+}(\text{T}^{4+}\square)\text{P}_2$ ,  $\text{M}^{3+}(\text{T}^{3+}\square)\text{P}_2$ ,  $\text{M}^{4+}(\text{T}^{2+}\square)\text{P}_2$ , and in chalcogenides like  $\text{M}^+(\text{T}^{3+}\square)\text{S}_2$ ,  $\text{M}^{2+}(\text{T}^{2+}\square)\text{S}_2$ ,  $\text{M}^{3+}(\text{T}^+\square)\text{S}_2$ . An ordered defect variant  $\text{M}(\text{T}_{3/2}^{2+}\square_{1/2})\text{X}_2$  might occur not only with  $\text{M} = \text{M}^+$ ,  $\text{X} = \text{S}, \text{Se}$ , as in orthorhombic ( $a = \sqrt{2} a_0$ ,  $b = \sqrt{8} a_0$ ,  $c = c_0$ )  $\text{Rb}_2\text{Zn}_3\text{S}_4$  and  $\text{Cs}_2\text{Zn}_3\text{S}_4$  [44] but also in pnictides ( $\text{M} = \text{M}^{3+}$ ,  $\text{X} = \text{P}, \text{As}, \dots$ ) like (hypothetic)  $\text{La}_2\text{Zn}_3\text{P}_4$ . A defect variant  $\square\text{T}_2^{2+}\text{S}_2$  or  $\square\text{T}_2^{3+}\text{P}_2$  does not occur with this kind of stacking.

Mooser–Pearson phases with X–X bonds ( $b_c = 0$ ,  $b_a = 1$ ) are possible in  $\text{ThCr}_2\text{Si}_2$ -type tetrelides  $\text{M}^{4+}\text{T}_2^+\text{X}_2$ ,  $\text{M}^{3+}(\text{T}^+\text{T}^{2+})\text{X}_2$ ,  $\text{M}^{2+}\text{T}_2^{2+}\text{X}_2$ ,  $\text{M}^+(\text{T}^{2+}\text{T}^{3+})\text{X}_2$  and pnictides  $\text{M}^{2+}\text{T}_2^+\text{X}_2$ ,  $\text{M}^{3+}(\text{T}^+\square)\text{X}_2$ .

It is tempting to speculate about the feasibility of defect variants like  $\square T_2^{3+}Si_2$ , e.g.  $AlSi$ , and  $\square T_2^{2+}P_2$ , e.g.  $ZnP$ , or  $\square T_2^+S_2$ , e.g. a nonmetallic modification of  $CuS$ .

Nonmetallic  $BaMg_2Sn_2$ -type representatives ( $b_c = 0$ ,  $b_a = \frac{1}{2}$ ) may be found among tetrelides of composition  $M^{4+}(T^+T^{2+})Si_2$ ,  $M^{3+}T_2^{2+}Si_2$ ,  $M^{2+}(T^{2+}T^{3+})Si_2, \dots$ , in pnictides  $M^{3+}T_2^+P_2$ ,  $M^{2+}(T^+T^{2+})P_2$ ,  $M^{2+}(T^{3+}\square)P_2$ ,  $M^+T_2^{2+}P_2$ , and in chalcogenides  $M^{2+}(T^+\square)S_2$ ,  $M^+T_2^+S_2$ ,  $M^+(T^{2+}\square)S_2, \dots$ , where the  $M(T, T')_2X_2$  and the  $M(T\square)X_2$  phases could crystallize in an ordered structure of lower symmetry.

In nonmetallic compounds the X–X pair distance should be close to the Pauling diameter. Based on pair distances observed in Mooser–Pearson phases, the following ranges appear to be reasonable: Si–Si =  $2.34 \dots 2.45$  Å, Ge–Ge =  $2.44 \dots 2.54$  Å, Sn–Sn =  $2.80 \dots 2.90$  Å, Pb–Pb =  $2.94 \dots 3.02$  Å, P–P =  $2.12 \dots 2.25$  Å, As–As =  $2.38 \dots 2.49$  Å, Sb–Sb =  $2.76 \dots 2.89$  Å.

### Comparison with experimental facts

Most uncertainties about the intrinsic conductivity character arise in connection with transition elements. Whether a transition-element compound will be a Mooser–Pearson phase or not strongly depends upon the electronegativity difference between T and X. In the case of the tetrelides this difference is small or even of the wrong sign. Thus, the essential assumption that Si and Ge act as anions may no longer be valid. The situation is not much better in the pnictides. Therefore, the formation of X–X pairs in certain tetrelides and pnictides is by no means an indication of bond saturation.

We will now review the known  $ThCr_2Si_2$ - and  $CaBe_2Ge_2$ -type phases in some detail, starting with the tetrelides. We can safely omit all phases where  $M = Ln^{3+}$  since they contain an odd number of valence electrons and therefore could be non-metallic only in the rare  $BaMg_2Sn_2$  structure.

The first transition element met in these structure types is chromium. The electron configuration of Cr is not favorable for tetrahedral coordination. Moreover, Si–Si pair distances of  $2.66$  Å are reported which are too large for single bonds, but too short to exclude any bonding. Therefore, we would not expect to find Mooser–Pearson phases among these chromium compounds, neither with  $M^{2+}$  nor with  $M^{4+}$ , in contradiction to the reported semiconductivity of  $ThCr_2Si_2$  [16]. In order for  $ThCr_2Si_2$  to be a Mooser–Pearson phase, the constant paramagnetism observed up to  $500$  K should be due to a low-spin (nonmagnetic)  $d^4$  configuration of Cr and an ‘ionic’ formula  $Th^{4+}Cr_2^{2+}Si_2^{4-}$  without Si–Si bonds which is rather unlikely. If its nonmetallic character can be confirmed then  $ThCr_2Si_2$  appears to be another non-Mooser–Pearson-type semiconductor like  $CrSi_2$ ,  $Mn_{26}Si_{47}$ ,  $FeSi_2$ ,  $Ru_2Si_3$ .

$MMn_2X_2$  tetrelides with divalent M atoms (Ca, Sr, Ba, Eu, Yb) are known for the germanides and one stannide (Ba) only [17]. The Ge–Ge distances range from  $2.60$  to  $2.74$  Å, which already points to metallic properties, since these distances are too short to exclude any X–X contacts as required for a normal valence compound  $M^{2+}Mn_2^{3+}X_2$  with a nonmagnetic  $d^4$  configuration of Mn. On the other hand, in  $BaMn_2Sn_2$  they are short enough (Sn–Sn =  $2.94$  Å) to represent a single bond, as required if we assume  $Mn^{2+}$  with a low-spin  $d^5$  configuration, which would be the tetrahedral analog to low-spin  $d^7$  of  $Co^{2+}$  in metallic  $CoS_2$ . The

compounds with rare-earth or actinide cations all order magnetically at ordering temperatures of  $300 \cdots 500$  K. The magnetic moments are between  $1.5 \cdots 3 \mu_B/\text{Mn}$ , i.e. the excess  $d$ -electrons are in a low-spin configuration, not in the high-spin  $d^5$  configuration adequate for nonmetallic compounds with tetrahedrally coordinated  $\text{Mn}^{2+}$ . The X–X pair distances in  $\text{ThMn}_2\text{Si}_2$  (2.57 Å) and  $\text{ThMn}_2\text{Ge}_2$  (2.61 Å) point to incompletely filled energy bands. The effective paramagnetic moments of 2.4 and  $2.3 \mu_B/\text{Mn}$ , resp. [18], would roughly agree with low-spin  $d^5$  or with band magnetism, and both lead to metallic properties.

$\text{EuFe}_2\text{Ge}_2$  appears to be the only known tetrelide with a divalent cation M and an iron-group T element. Fe is reported to have a spin-paired  $d^6$  configuration [19] which is expected rather in octahedral coordination unless the ionic charges are reversed. The nonmagnetic state of the more electronegative Ru and Os in the corresponding tetrelides then was to be expected. If the T element acts as an anion then again  $\text{M}^{2+}\text{Fe}_2\text{Si}_2$  and  $\text{M}^{2+}\text{Fe}_2\text{Ge}_2$  as well as  $\text{ThFe}_2\text{Si}_2$ ,  $\text{ThRu}_2\text{Si}_2$  and  $\text{ThOs}_2\text{Si}_2$  cannot be Mooser–Pearson phases, even if they turned out to be nonmetallic. The latter two are not superconducting down to 1.6 K and have an  $n$ -type thermopower of  $\sim 5 \mu\text{V/K}$  at room temperature, according to own measurements.

A nonmagnetic state of the T atoms is observed also in the Co-group and in the Ni-group tetrelides. In  $\text{CaCo}_2\text{Ge}_2$  the Ge–Ge distance is 2.65 Å, similar to the case of  $\text{CaNi}_2\text{Ge}_2$  (2.61 Å [17]), from which we deduce metallic properties.

Queer enough, X–X distances in the single-bond range ( $b_a = 1$ ) are reported for the metallic compounds  $\text{DyCo}_2\text{Si}_2$  (2.34 (?) [20, 21] or 2.491 Å [22]),  $\text{Yb}^{3+}\text{Co}_2\text{Si}_2$  (2.323 Å [20]),  $\text{TbNi}_2\text{Si}_2$  (2.443 Å [23]),  $\text{CePd}_2\text{Si}_2$  (2.377 Å [24]). In  $\text{ThCo}_2\text{Ge}_2$  Ge–Ge = 2.543 Å [16] and in  $\text{ThNi}_2\text{Ge}_2$  Ge–Ge = 2.57 Å [16]. The configuration  $\text{Th}^{4+}\text{Co}_2^+\text{Ge}_2$  would account for Ge pairs and leaves an even number of  $d$ -electrons per Co atom, but this is not a stable configuration and band overlap would certainly occur. In the corresponding nickel compound Ni then should carry one more (an odd) electron. The superconductivity [25] reported for  $\text{YbPd}_2\text{Ge}_2(\text{r})$  (where Ge–Ge  $\approx 2.51$  Å from the given approximate  $z$ -value [26]) is an experimental proof for the metallic character of  $\text{M}^{2+}\text{Pd}_2\text{X}_2$  tetrelides.

The Cu-group tetrelides, which are also nonmagnetic, differ from the preceding analogs insofar as the values of the  $c$ -axis and the axial ratio  $c/a$  show an increase on going to smaller  $\text{M}^{3+}$  cations [4]. In  $\text{CaCu}_2\text{Si}_2$  and  $\text{SrCu}_2\text{Si}_2$  the distance within the Si pairs is 2.32 and 2.42 Å, respectively [27], i.e. well within the range for single bonds. The same holds for the germanides  $\text{CaCu}_2\text{Ge}_2$  (2.476 Å),  $\text{CaAg}_2\text{Ge}_2$  (2.43 Å),  $\text{SrAg}_2\text{Ge}_2$  (2.48 Å) [27],  $\text{CaAu}_2\text{Ge}_2$  (2.48 Å),  $\text{SrAu}_2\text{Ge}_2$  (2.46 Å) [28], and even for the stannides  $\text{SrAg}_2\text{Sn}_2$  (2.79 Å [17]) and  $\text{BaAg}_2\text{Sn}_2$  (2.81 Å [28]). In these representatives with formal valences  $\text{M}^{2+}\text{T}_2^+(\text{X}_2)^{6-}$  two cation electrons are lacking for bond saturation.  $\text{ThCu}_2\text{Si}_2$  (Si–Si = 2.38 Å [16]),  $\text{ThCu}_2\text{Ge}_2$  and  $\text{UCu}_2\text{Ge}_2$  (Ge–Ge = 2.454 [16] and 2.387 Å, respectively), on the other hand, fulfill the electron criterion for nonmetallic  $\text{M}^{4+}\text{T}_2^+(\text{X}_2)$  tetrelides, if at all it is reasonable to assign these valences. The electronegativity differences as well as the Th–Cu distances (in  $\text{ThCu}_2\text{Si}_2$  and  $\text{ThCu}_2\text{Ge}_2$  Th–Cu = 3.21 and 3.28 Å, respectively, as compared with 3.05 and 3.07 Å in  $\text{ThCu}_2$  and  $\text{Th}_2\text{Cu}$ , respectively) probably make semiconductivity impossible. An own sample of  $\text{ThCu}_2\text{Si}_2$  which was not pure enough for the semiconductivity test did not show superconductivity either ( $T_n = 1.6$  K). In the



heavy-fermion superconductor  $CeCu_2Si_2$  Ce is not tetravalent but of intermediate valence, and superconductivity appears to depend in a delicate manner on copper concentration [45, 46] (and Cu/Si disorder?).

The phases with Be, Mg, Zn and Cd (like those with Cu) put no problem as regards the valence of the tetrahedral element T ( $=T^{2+}$ ). In  $CaBe_2Ge_2$ , however, we would expect the  $ThCr_2Si_2$  structure with X–X pairs but surprisingly  $CaBe_2Ge_2$  is just the prototype of that  $BaAl_4$  derivative structure without X–X pairs [12]. Therefore it must be metallic. Certain alkaline-earth tetrelides  $M^{2+}T_2^{2+}X_2$  with T = Mg, Zn, Cd have some chance to be Mooser–Pearson phases. The binary tetrelides  $Ca_2X$ ,  $Sr_2X$ ,  $Ba_2X$  and  $Mg_2X$ , with X = Si, Ge and Sn, are all semiconducting, which indicates that at least with T = Mg the electronegativity differences are favorable. In  $BaMg_2Si_2$  and  $BaMg_2Ge_2$  the distances within the X–X pairs (2.484 and 2.58 Å, respectively [27]) are somewhat long but in  $CaZn_2Ge_2$  and  $SrZn_2Ge_2$  the Ge–Ge distances (2.47 [27] and 2.50 Å [29], respectively) are close to the value expected for a single bond. This may even hold for  $SrCd_2Ge_2$  with Ge–Ge = 2.54 Å [28]. The high electronegativity value of Zn and Cd, however, may be a handicap.  $BaMg_2Sn_2$  [14] and  $BaMg_2Pb_2$  [14], on the other hand, both certainly cannot be Mooser–Pearson phases. The latter crystallizes in the  $CaBe_2Ge_2$  structure where no X–X pairs occur ( $b_a = 0$ ), while the former is the prototype of a 1:1 mixture of the  $ThCr_2Si_2$  and  $CaBe_2Ge_2$  type, i.e. it can at best contain half the necessary X–X pairs ( $b_a = \frac{1}{2}$ ).

Surprisingly, in the  $M^{2+}T_2^{3+}X_2$  tetrelide  $SrAl_2Pb_2$  [28] the Pb–Pb distance 2.73 Å is even below the single-bond value although the formula would point to a normal valence compound. Thus  $SrAl_2Pb_2$  too is metallic.

It is noteworthy that with Ba, Mg and Si, Ge, nonmetallic layered compounds are possible with different stoichiometries: The normal valence compounds  $BaMgSi$  and  $BaMgGe$  adopt the  $PbFCl$ -type structure with two Ba layers between the  $[MgSi_{4/4}]_\infty$  tetrahedron sandwiches [27]. The unique stacking in the  $ThCr_2Si_2$ -type structure allows a localisation of the two excess valence electrons in  $BaMg_2Si_2$  and  $BaMg_2Ge_2$ . One might expect a similar correspondence with T = Zn, Cd. It occurs also for a few metallic tetrelides:  $GdMnSi$ – $GdMn_2Si_2$ ,  $LnFeSi$ – $LnFe_2Si_2$ ,  $LnCoSi$ – $LnCo_2Si_2$ .

Let us turn now to the pnictides. Many of the normal valence compounds crystallize in the trigonal  $La_2O_2S$  structure. As in  $La_2O_2X$  a transition to the tetragonal structure takes place with increasing size of the minority atom:  $La_2O_2S$ ,  $La_2O_2Se$  (trigonal)– $La_2O_2Te$  (tetragonal), corresponding to the series  $CaMn_2P_2(As_2)$ ,  $SrMn_2P_2(As_2)$  (trigonal)– $BaMn_2P_2(As_2)$  (tetragonal).

In the alkaline-earth pnictides with large X–X distances the T atom must be divalent and the T–4T distances within the T square layers should be large enough to exclude any bonding ( $b_a = b_c = 0$ ). In  $BaZn_2P_2$  no P–P bonding occurs (P–P = 3.685 Å) as expected, however, Zn–4Zn = 2.842 Å [30], which is rather close to the distance in metallic zinc (2.70 Å) and thus could induce semimetallic properties. Strikingly,  $BaZn_2As_2$  adopts the  $BaCu_2S_2$  structure where no such close T–T contacts occur.

$BaMn_2P_2$  [31],  $BaMn_2As_2$  [32],  $BaMn_2Sb_2$ ,  $CaFe_2P_2$ ,  $SrFe_2P_2$ ,  $BaFe_2P_2$  [31],  $EuFe_2P_2$  [34],  $SrFe_2As_2$ ,  $BaFe_2As_2$  [33] all show no X–X contacts as expected for normal valence compounds, but we hesitate to assume that divalent Mn or Fe would be stable in these compounds. The same holds for  $SrCo_2P_2$  [31],  $EuCo_2P_2$  [34],  $EuCo_2As_2$ ,  $SrCo_2As_2$ ,  $BaCo_2As_2$  [33],  $BaNi_2P_2$  [47] and  $BaNi_2As_2$  [33]. In

$\text{CaNi}_2\text{P}_2$  [33] ( $\text{P-P} = 2.297 \text{ \AA}$ ), on the other hand, some P-P bonding certainly exists. As Mewis [47] pointed out the X-X distances strongly depend on the size of the M element.

Magnetic measurements show Pauli paramagnetism in  $\text{CaNi}_2\text{As}_2$ ,  $\text{SrNi}_2\text{As}_2$  and  $\text{BaNi}_2\text{As}_2$  [33].  $\text{Ni}^{2+}$  can adopt a nonmagnetic  $d^8$  configuration in square-planar coordination (e.g. in the monoclinic modification of  $\text{NiP}_2$  which is a Mooser-Pearson phase with  $b_a = 2$ ), but here we take the absence of a localized moment as an indication of metallic behavior.

The copper compounds, where  $\text{Cu}^+$  nicely fits into tetrahedral coordination, have indeed close X-X contacts:  $\text{P-P} = 2.25, 2.30, 2.28 \text{ \AA}$  for  $\text{MCu}_2\text{P}_2$  [31], with  $\text{M} = \text{Ca}, \text{Sr}, \text{Eu}$ , respectively, and  $\text{As-As} = 2.51 \text{ \AA}$  for both  $\text{SrCu}_2\text{As}_2$  and  $\text{BaCu}_2\text{As}_2$  [33]. These distances are rather at the upper limit, but at least  $\text{CaCu}_2\text{P}_2$  might be a Mooser-Pearson phase.  $\text{SrCu}_2\text{Sb}_2$  [35], on the other hand, crystallizes in the  $\text{CaBe}_2\text{Ge}_2$  structure ( $b_a = 0$ ) and therefore must be metallic.

Several  $\text{ThCr}_2\text{Si}_2$ -type pnictides are known with the large cation being an alkali element [36]. In compounds with an odd number of valence electrons one excess anion electron (as in  $\text{M}^+\text{T}_2^{2+}\text{P}_2$ ) could be bound if the  $\text{BaMg}_2\text{Sn}_2$  structure were adopted. Then again nonmetallic analogs like  $\text{LiFeAs-LiFe}_2\text{As}_2$ ,  $\text{NaMgAs-NaMg}_2\text{As}_2$ ,  $\text{KMnP-KMn}_2\text{P}_2$  with anti-PbFCl-type vs.  $\text{BaMg}_2\text{Sn}_2$ -type structure might exist in analogy to the Ba-Mg-Si system.

In  $\text{ThCr}_2\text{Si}_2$ -type  $\text{LiCu}_2\text{P}_2$  three excess anion valence electrons per formula unit should be bonded in X-X bonds, so that in spite of the very short P-P distance of  $2.14 \text{ \AA}$  [37] there remains an incompletely filled valence band. The same valence-electron mismatch exists in  $\text{CeLi}_2\text{Sb}_2$ ,  $\text{PrLi}_2\text{Sb}_2$  and  $\text{NdLi}_2\text{Sb}_2$  [38] which crystallize in the  $\text{CaBe}_2\text{Ge}_2$  structure while the  $\text{BaMg}_2\text{Sn}_2$  type would be adequate.

The only group where it is fairly safe to predict the conductivity character is the group of the chalcogenides. Up to now no chalcogenide with X-X bonds was found. The compounds with formulas according to the simple valence rules are all semiconducting [39, 40]. There is no danger of close X-X contacts since  $c/a > 3$  for all known chalcogenides. Several metallic  $\text{Tl}^+\text{T}_2\text{X}_2$  phases are known [41, 42]. By substituting part of the T atoms the electron balance and hence nonmetallic properties can be attained. In  $\text{TlCu}_{3/2}\text{Fe}_{1/2}\text{S}_2$  and  $\text{Tl}^+\text{Fe}^{3+}\square\text{S}_2$  trivalent Fe is probably in a high-spin state which is neutral as regards crystal-field effects. In  $\text{KLiFeS}_2$  [43], which probably also crystallizes in the  $\text{ThCr}_2\text{Si}_2$  structure (if disordered), Fe is divalent, so that we think  $\text{Mn}^{2+}$  with high-spin  $d^5$  configuration in hypothetical  $\text{KLiMnS}_2$  would be even more appropriate.

As a result of this reviewing we got the impression that nonmetallic properties may establish rather occasionally in the group of  $\text{MT}_2\text{X}_2$  pnictides and tetrelides. The  $\text{ThCr}_2\text{Si}_2$  structure as well as the related structures are not adopted in order to attain nonmetallic properties. On the contrary, several compounds obviously prefer that crystal structure which makes semiconductivity impossible. This is the case for the prototypes  $\text{BaMg}_2\text{Sn}_2$  and  $\text{CaBe}_2\text{Ge}_2$  which clearly demonstrate that they favor the metallic state. On the other hand, these structures are not favorable for high- $T_c$  superconductivity either.

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