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## THEORY OF THE PHASE TRANSITION IN IV-VI COMPOUNDS (\*)

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**Résumé.** — La théorie thermodynamique des transitions de phase du second ordre dans les cristaux avec les modifications et les simplifications faites récemment par l'auteur et ses collaborateurs, est appliquée à la structure du sel gemme pour prédire plusieurs phases de plus basse symétrie réalisables par des transitions de déplacement du second ordre qui ne changent pas la cellule unité, en plus de la structure trigonale vue dans GeTe. Nous proposons un modèle microscopique pour de telles transitions qui impliquent une instabilité configurationnelle de groupe d'espace (Jahn-Teller) d'un modèle proposé pour les liaisons de valence dans ces composés. Nous donnons des propositions de vérifications expérimentales de ces hypothèses.

**Abstract.** — The thermodynamic theory of second order phase transitions in crystals with the modifications and simplifications recently made by the author and co-workers is applied to the rocksalt structure. We predict several lower symmetry phases achievable via second-order displacive transitions which do not change the unit cell, in addition to the trigonal structure seen in GeTe. A microscopic model is proposed for such transitions, involving space-group configurational (Jahn-Teller) instability of a proposed valence-bond model of electronic structure of binding of these compounds. Some experimentally verifiable tests of these proposals are given.

**1. Introduction.** — In this paper a theory of the phase transition in IV-VI Compounds will be given. The paper consists of two parts.

First, the thermodynamic theory of second order phase transitions in crystals is applied to rocksalt structure. It is found that several lower symmetry space groups can be achieved by second order phase transition without change of unit cell. One of these, the trigonal (rhombohedral) has been observed in GeTe. The others are new predictions. It is found that the transformation from rocksalt may be driven by the physical tensor field of the optic mode displacements.

Secondly a proposal is made that the observed GeTe phase transition represents a space group configurational instability. It is proposed that cohesion in the GeTe structure be understood on the basis of valence bonds. The phase transition is then a configurational instability of such bonds with respect to the optic mode displacement.

Experiments are proposed to test these results and proposals.

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**2. Theory.** — In the thermodynamic theory [1] of second order phase transitions in crystals attention is focussed upon two interrelated basic quantities describing the state of the crystal : the thermodynamic potential  $\Phi$  and the density function  $\rho$ . Both  $\Phi$  and  $\rho$  are functions of temperature, pressure, and some set of order parameters  $\{c_\alpha^{(k_\sigma)(m)}\}$ . The density function is also a function of position in the crystal, so we may write

$$\Phi(T, P, \{c_\alpha^{(k_\sigma)(m)}\}) \quad (2.1)$$

and 
$$\rho(\mathbf{r}, \{c_\alpha^{(k_\sigma)(m)}\}) . \quad (2.2)$$

If the density function  $\rho$  of the crystal is specified, then one may determine the corresponding symmetry group of the crystal :  $\mathcal{G}$  : it is the invariance group of  $\rho(\mathbf{r})$ , and consists of all transformations of space which send the crystal into itself.

Let  $\mathcal{G}_0$  be the symmetry group of the high symmetry phase. Then a set of order parameters can be defined by first considering the set of all functions  $\{\psi_\alpha^{(k_\sigma)(m)}(\mathbf{r})\}$  where  $\psi_\alpha^{(k_\sigma)(m)}(\mathbf{r})$  belongs to the  $\alpha^{\text{th}}$  row of the irreducible representation  $D^{(k)(m)}$  of  $\mathcal{G}_0$ . We write the density function as :

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \sum_{\alpha} c_\alpha^{(k_\sigma)(m)} \psi_\alpha^{(k_\sigma)(m)}(\mathbf{r}) . \quad (2.3)$$

In (2.3) only the members of one single irreducible

representation appear, as will be later emphasized, and the  $c_{\alpha}^{(k_{\sigma})(m)}$  are coefficients which are dependent upon  $T$  and  $P$ . The  $c_{\alpha}^{(k_{\sigma})(m)}$  will be the order parameters in  $\Phi$ . In (2.3)  $\rho_0(\mathbf{r})$  is invariant under  $\mathcal{G}_0$ , and  $\rho(\mathbf{r})$  will be characterized by an invariance group  $\mathcal{G}$ . If some  $c_{\alpha}^{(k_{\sigma})(m)} \neq 0$  then  $\mathcal{G}$  is not isomorphic to  $\mathcal{G}_0$ . Instead of considering the functions  $\psi_{\alpha}^{(k_{\sigma})(m)}(\mathbf{r})$  to transform amongst themselves, we consider the  $c_{\alpha}^{(k_{\sigma})(m)}$  to be so transformed.

The representation  $D^{(k)(m)}$  used in (2.3) corresponds to a single physical tensor field [2]. If the tensor field transforms reducibly (for example, the strain tensor  $[\sigma]$  in a cubic crystal) then only one irreducible component appears in (2.3).

For the thermodynamic potential  $\Phi$ , we write an expansion into a series of scalar homogeneous polynomials in the order parameters :

$$\Phi = \Phi^{(0)} + \Phi^{(1)} + \Phi^{(2)} + \dots + \Phi^{(s)} + \dots \quad (2.4)$$

when  $\Phi^{(s)}$  is of  $s^{\text{th}}$  degree in the  $\{c_{\alpha}^{(k_{\sigma})(m)}\}$ . The thermodynamic potential  $\Phi$  applies to the system in high and low symmetry states. At given  $T$  and  $P$ , the non-vanishing  $\{c_{\alpha}^{(k_{\sigma})(m)}\}$  in  $\Phi$  and  $\rho$ , are determined by requiring that  $\Phi$  shall be a minimum ; the minimum must correspond to symmetry  $\mathcal{G}_0$  above the transition  $(T, P) > (T_c, P_c)$ , and to a lower symmetry  $\mathcal{G}_1$  below the transition  $(T, P) < (T_c, P_c)$ . Then for  $(T, P) > (T_c, P_c)$  we must have the stable situation : all  $c_{\alpha}^{(k_{\sigma})(m)} = 0$ , giving minimum  $\Phi$ . For  $(T, P) < (T_c, P_c)$  the stable situation must correspond to some  $c_{\alpha}^{(k_{\sigma})(m)} \neq 0$ , and therefore from Equation (2.3) :  $\rho(\mathbf{r}) \neq \rho_0(\mathbf{r})$ .

A transition from  $\mathcal{G}_0$  to  $\mathcal{G}_1$  can occur continuously as a second order transition if

$$\mathcal{G}_1 \text{ is a subgroup of } \mathcal{G}_0. \quad (2.5)$$

If  $c_{\alpha}^{(k_{\sigma})(m)} = 0$  is stable for  $\Phi$  above  $(T_c, P_c)$  we require that the linear, cubic, ... terms in (2.4) shall vanish identically, or that the symmetrized cube of  $D^{(k)(m)}$  shall not contain the identity :

$$([\ast \mathbf{k} m]_{(3)} | \Gamma^{(1+)}) = 0. \quad (2.6)$$

For the groups  $\mathcal{G}_1$  and  $\mathcal{G}_0$  to be compatible via second order phase transition driven by the acceptable representation  $D^{(k)(m)}$  it is required that [3]

$$D^{(k)(m)} \text{ of } \mathcal{G}_0 \text{ subduces } D^{(\Gamma)(1+)} \text{ of } \mathcal{G}_1. \quad (2.7)$$

To eliminate superfluous lower symmetry groups, a chain criterion also can be proven [4] :

$$\begin{aligned} &\text{if} && \mathcal{G}_0 \supset \mathcal{G}_1 \supset \mathcal{G}'_1 \\ &\text{and } D^{(k)(m)} \text{ of } \mathcal{G}_0 \downarrow D^{(\Gamma)(1+)} \text{ of } \mathcal{G}_1 \text{ (once)} \\ &\text{and } D^{(k)(m)} \text{ of } \mathcal{G}_0 \downarrow D^{(\Gamma)(1+)} \text{ of } \mathcal{G}'_1 \text{ (once)} \\ &\text{then} && \mathcal{G}_0 \rightarrow \mathcal{G}'_1 \text{ is eliminated.} \end{aligned} \quad (2.8)$$

The novel general aspects of our recent work [2], [3], [4] are : the emphasis on using a concrete physical tensor field for  $D^{(k)(m)}$ , and equations (2.7), (2.8). Early applications of the thermodynamic theory [5] did not insist upon using a physical field, nor did they have available (2.7), (2.8). With these results, plus equations (2.5) and (2.6), detailed and concrete predictions can be made regarding symmetry changes which may occur from  $\mathcal{G}_0$ .

**3. Phase Transition in IV-VI Systems with Rocksalt Structure.** — For a displacive second-order phase transition in GeTe-type systems [6] without change of unit cell we choose the physical field involved to be that of the atom displacements in the optic normal mode at  $\mathbf{k} = \Gamma = (0, 0, 0)$  in the high temperature cubic rocksalt structure [7]. This mode is of the symmetry of a polar vector :  $\Gamma^{(15)}$ . Since

$$([\Gamma 15]_{(3)} | \Gamma 1+) = 0 \quad (3.1)$$

the representation is acceptable, i. e. meets the criterion (2.6), related to stable equilibrium of the rocksalt structure. Using this physical field means that we shall obtain lower symmetry space groups which are related by relative motion (inner strain) of the Ge and Te sub-lattices. To obtain the axial distortions which also can occur, in trigonal, or tetragonal etc. systems, requires including the effect of the strain field  $[\sigma]$ . This will be done later.

Using criterion (2.5), it is found [8] that there are 32 « equi-translation » sub-space groups of the rocksalt structure  $O_h^5$ . Each of these is a candidate, in principle, for lower symmetry space group achievable via second order transition.

Now we combine the acceptable representation  $\Gamma^{(15)}$  with the potential sub-space groups. The subduction criterion (2.7) can be simply applied to this case. We ask : on which of the 32 « equi-translation » sub-space groups of  $O_h^5$  will  $\Gamma^{(15)}$  of  $O_h^5$  subduce  $\Gamma^{(1+)}$  (the identity representation) ? Since the translation group is unchanged, it does suffice to concern ourselves only with the point group of each such sub-space group : these are the corresponding factor groups  $\mathcal{G}/\mathcal{J}$ . Straightforward examination of the relevant character tables reveals 8 possibilities given in

Table I. Application of the chain subduction criterion reduces these further, as is shown in Table II.

TABLE I		
Subgroups of $O_h^5$ - $Fm3m$ Consistent with Subduction Criterion		
Class	Space Group	
Trigonal	$C_{3v}^5 - R3m$	$C_3^4 - R3$
Tetragonal	$C_{4v}^9 - I4mm$	$C_4^5 - I4$
Orthorhombic	$C_{2v}^{20} - Imm2$	$C_{2v}^{18} - Fmm2$
Monoclinic	$C_2^3 - B2$	or $C2$
	$C_s^3 - Bm$	or $Cm$

TABLE II  
Compatible Subgroups of  $O_h^5$ - $Fm3m$

Class	Space Group
Trigonal	$C_{3v}^5 - R3m$
Tetragonal	$C_{4v}^9 - I4mm$
Orthorhombic	$C_{2v}^{20} - Imm2$
	$C_{2v}^{18} - Fmm2$
Monoclinic	$C_v^3 - B2$ or $C2$
	$C_s^3 - Bm$ or $Cm$

A compatible sub-space group is  $C_{3v}^5 - R3m$ , which is the trigonal group that has been observed [9]. In addition, tetragonal orthorhombic, and monoclinic sub-space groups are predicted. These possibilities besides the trigonal, require examination on the basis of the dynamics of the displacements which might produce the distorted structure.

The major conclusions to be drawn from this examination of the GeTe phase transition from the viewpoint of the thermodynamic theory are :

1. The optic mode displacements at long wave length of symmetry  $\Gamma^{(15)}$  may be identified as the irreducible physical tensor field driving the second order phase transition from the rocksalt structure. This field is fully consistent with the requirements of the thermodynamic theory.

2. The observed trigonal space group, as well as others listed in Table II, can arise via second order phase transitions without change of unit cell.

To obtain the axis distortion (i. e.  $c/a \neq 1$ ) in various lower symmetry cases of GeTe, it is necessary

to include the strain tensor  $[\sigma]$ . In a cubic space group this field transforms as [10]

$$[\sigma] \approx A_{1g} \oplus E_g \oplus F_{2g}.$$

Let us illustrate the nature of the necessary analysis on the trigonal group. To obtain a trigonal distortion requires use of the shears in  $F_{2g}$ . Then the form of  $\rho(r)$  will be

$$\rho(r) = \rho_0(r) + [F_{1u}] + [F_{2u}] \quad (3.2)$$

where the notation indicates which of the irreducible  $D^{(k)(m)}$  contribute « order parameters ». The corresponding expression for the thermodynamic potential  $\Phi$  will be given, also using a symbolic notation, as :

$$\begin{aligned} \Phi = & \Phi^0 + A(P, T) [F_{1u}]_{(2)} + C(P, T) [F_{1u}]_{(4)} + \dots \\ & + A'(P, T) [F_{2g}]_{(2)} + \dots \\ & + D(P, T) ([F_{1u}]_{(2)} \otimes F_{2g}) + \dots \end{aligned} \quad (3.3)$$

In (3.3) the first line represents the expansion of  $\Phi$  in the order parameter, like (2.4), with

$$A(P_c, T_c) = 0 \quad (3.4)$$

determining the line of second order phase transitions. The second line in (3.3) represents normal elastic energy density. The last line represents a coupling of elastic distortion and inner strain : it occurs because an invariant can be constructed from

$$[F_{1u}]_{(2)} \otimes F_{2g}$$

and will then appear in (3.3). It is easy to prove that minimizing (3.3)  $T, P < T_c, P_c$  will produce a non-zero inner strain displacement plus a coupled macroscopic shear strain. Thus while the  $T$  and  $P$  on the line of second order phase transitions is determined by (3.4), the full thermodynamic potential  $\Phi$  of (3.3) including coupling, is needed to obtain the lower symmetry group (in this case the trigonal group  $C_{3v}^5$ ), *in toto* [11].

**4. Mechanism of the Phase Transition.** — a) CONFIGURATIONAL INSTABILITY OF VALENCE-BONDS. — Let us examine a configurational instability mechanism [12] for the phase transition from rocksalt structure driven by the  $\Gamma^{(15)}$  optic mode. In examining this proposal we use a localized (valence-bond) formulation, as the Bloch (molecular orbital) formulation cannot give the required effect owing to vanishingly small values of the integrals which arise [13] ; this necessitates summing up such contributions over an *entire* partially filled valence bond, which is very inconvenient (see **Discussion** at the end of the paper). In the rocksalt structure each atom of Ge is surrounded by 6 first neighbor atoms of Te at the corners

of a regular octahedron. All 6 bond lengths are equal, all bond angles are  $90^\circ$ . It has been suggested [14] that the bonding here is : pure  $p^3$  bonds from each ligand to the other (in Ge  $4p$ ; in Te  $5p$ ). These orbitals have the requisite angular property, but are not the optimum equivalent octahedral set [15]. To test the suitability of these orbitals we form the symmetrized square of their representation. The  $p$  orbitals transform as  $[F_{1u}]$ . The symmetrized square  $[F_{1u}]_{(2)}$  only contains even orbitals, hence  $p$  states (even if partially filled as in the present case) are not configurationally unstable in  $O_h$  configuration.

A better set of localized orbitals [16] are the hybridized octahedral orbitals  $sp^3 d^2$ . These are to be composed from Ge  $4s 4p 4d$  and from Te  $5s 5p 5d$ . The two atoms per cell contribute 10 electrons to these hybrids : there must then be some « resonance » amongst the 2 unoccupied hybrid orbitals. Owing to the larger energy separation [17] between Ge  $4s$  and  $4p-4d$  states than the Te  $5s$  to  $5p-5d$  separation, we may assume that the residual instability of the rocksalt structure in this case is related to the energy cost of promoting the Ge  $4s$  electron. The use of  $d$  orbitals in forming hybrid bond orbitals in metals and alloys was already proposed [18].

The hybridized octahedral valence bond orbital  $sp^3 d^2$  is unstable with respect to distortion based on a normal mode of symmetry  $F_{1u}$ . This result was recently proved by us [19], for molecules of  $O_h$  symmetry, and the proof applies here without modification. Initially the 6 bond orbitals per atom are degenerate (call the energy  $E_0$ ). Then define the matrix elements

$$\alpha \equiv (s | \Gamma^{(15)} | p); \quad \beta \equiv (p | \Gamma^{(15)} | d)$$

which are matrix elements of the electron-ion interaction in the normal mode  $\Gamma^{(15)}$ . Then call

$$c_1 = 2\beta/6^{1/2} + 3\alpha/\sqrt{3}; \quad c_2 = 2\beta/\sqrt{6}.$$

Now if [20]

$$\alpha \approx 0; \quad c_1 = c_2$$

then the perturbed spectrum for a trigonal distortion of the octahedron is

$$E^+ = E_0 + c_1 Q + kQ^2/2 \quad (\text{three times})$$

$$E^- = E_0 - c_1 Q + kQ^2/2 \quad (\text{three times}).$$

Here  $Q$  is the amplitude of the trigonal distortion based on  $F_{1u}$  mode, and  $k$  an ordinary bond spring constant. The perturbed equilibrium values of  $Q$  are obtained easily by differentiation. Clearly we obtain in this fashion 2 sets of three degenerate states each.

With 10 electrons available, the lower 5 states are occupied, resulting in a net lowering of energy. In fact the minimum energy in each case corresponds to

$$E^\pm(\min) = E_0 - c_1/k + c_1^2/2k$$

with

$$Q = -c_1/k \quad \text{or} \quad +c_1/k.$$

Hence in three cases we have a positive space trigonal displacement, in three cases a negative trigonal displacement.

We interpret these results as showing that configurational instability tends to lengthen three bonds and shorten three others, to produce a new stable equilibrium which involves the trigonal distortion of the octahedron. The energy gain on distortion in this fashion (5 filled orbitals) is approximately

$$-(2c_1/k)$$

in appropriate units. We have not determined the new bond eigenfunctions (eigenvectors) corresponding to these eigenvalues, but we take them to be consistent with observed distortions in GeTe (see next paragraph).

#### b) STRUCTURE OF GeTe, AND VALENCE BONDS. —

For preliminary confirmation of these results, we consider the array around each atom in the distorted GeTe structure [6]. The six formerly equivalent octahedral bonds are now divided into two groups of three. Three bonds are shorter, three bonds longer. Ratio of the lengths (first neighbor distances) are : 0.662/0.735. The geometrical configuration of these six bonds is that of two trigonal prisms sharing a common apex (formerly the center of the octahedron). Bond angles were formerly all  $90^\circ$ . Now the angle between two short bonds is  $92^\circ 30'$ ; the angle between two long bonds is  $81^\circ 50'$ . The long-short bond angle is  $90^\circ 20'$ . These numbers were obtained using the room temperature parameter values [6] for GeTe of : rhombohedral angle  $\alpha = 57^\circ 14'$ , relative parameter  $u = 0.237$ .

It will be recalled that one cannot obtain a bond angle of less than  $90^\circ$  by use of  $s$  and  $p$  orbitals alone [21]. However, angles of greater than  $90^\circ$  can be obtained by  $s$  and  $p$ , or by  $p$  and  $d$ . As a significant key to what is going on, we must consider the bond angle of  $81^\circ 50'$ . It is possible to obtain three equivalent trigonal prism bonds which are orthogonal, and make this angle with one another by eliminating the «  $s$  » contribution to these bonds, and constructing bonds with nominal composition  $d^2 p$ . For the other

three equivalent trigonal prism bonds at angle  $92^\circ 30'$  some admixture of «  $s$  » atomic state remains necessary [22].

In summary our picture of the bonding in GeTe utilizes some established principles of chemical valence theory. We assume the octahedral bonds are not pure  $p^3$ , but the « strong »  $sp^3 d^2$  hybrids. In the rhombohedral structure one set of trigonal bonds (weaker) is of type  $pd^2$ , the other (stronger) is composed of some  $s-p-d$  hybrid.

This picture is consistent with configurational instability in GeTe. We may assume that the transition temperature (650 °K) in this material is determined as the temperature below which sufficient  $4s$  eigenfunction cannot be incorporated (« promoted ») into the Ge bonds to produce strong octahedral bonds. So then the instability dominates, and the structure distorts with concomitant change in the nature of the bond hybrids. We may assume throughout that the Te atom  $sp^3 d^2$  bond hybrids are always available owing to the closer proximity of  $5s$  state to  $5p-5d$  in Te. This point of view will be relevant to the discussion of structure of (GeSn) Te alloys below.

c) THE (GeSn) Te ALLOYS. — Addition of SnTe to GeTe stabilizes the rocksalt structure [9]. Pure SnTe seems not to undergo a phase transition to a lower symmetry structure. The picture presented above is consistent with these observations. Thus, Sn is in the same row of the periodic chart as Te and the  $5s$  energy level separation from  $5p$  and  $5d$  is the same in Sn and Te. Consequently Sn atoms form strong  $sp^3 d^2$  octahedral bonds as easily as Te. The addition of SnTe replaces a fraction of the Ge sites by Sn and produces strong octahedral bonds which occupy that fraction of the replaced sites. These bonds are also unstable in regard to the  $F_{1u}$  mode. It may be assumed however that motional averaging [23] (« dynamic Jahn-Teller Effect ») over equivalent trigonally distorted configurations prevents a finite distortion in pure SnTe. The added factor of the difference of promotion energy between  $4s$  and  $4p-4d$  and  $5s$  and  $5p-5d$  is absent, compared to GeTe, leading to stabilization.

**5. Discussion and Proposed Experiments.** — What are the observable consequences of the analysis given here ?

As a result of the application of the thermodynamic theory of second order phase transitions we predicted several new lower symmetry structures accessible by second order phase transitions to the systems initially

in rocksalt structure. These should be sought experimentally.

Also, by using the complete theory, it was verified that the optic mode  $\Gamma^{(15)}$  is acceptable by the criteria of the theory. This puts added theoretical support to the proposal recently made that this mode drives the transition in GeTe. The proposal was made on the basis of lattice dynamics [7]. To date, experiments have been reported for SnTe, which demonstrate « softening » of this mode ; however SnTe does not undergo transition from rocksalt structure [7].

The proposal that partially filled valence bonds play a role in the binding may have observable consequences in regard to the magnetic properties of GeTe, SnTe and their alloys. We would anticipate paramagnetic susceptibility associated with the partially filled bonds [24].

Observation of Knight shift, or direct NMR studies [25] in the GeTe and SnTe lattices in both cubic and other structures could reveal some quantitative information about valence bond composition in conjunction with the phase transition. We anticipate departure from the pure  $p$  atomic orbitals and possibility of computing  $s$  and  $d$  contributions to the bond eigenfunctions.

A final proposal for experiments relates to SnTe. Our theory is that the rocksalt structure for this material, is susceptible to configurational instability, but is stabilized by « motional averaging », even at low temperatures. This should produce anomalously large « Debye-Waller » temperature factors [26] for the ions in X-Ray scattering. Especially at low temperature, it would be desirable to measure these temperature factors in SnTe, and attempt a quantitative comparison with a theoretical estimate which neglects contribution due to configurational instability. This quantitative intercomparison could validate the anomalously large amplitude of ion motion which would be predicted for motional averaging.

At this point, it may be worthwhile to emphasize that our adoption of a valence bond approach in Section 4 is the result of our attempt to describe the phase transition as configurational instability. In this description we are attempting to determine the microscopic or electronic basis for the « soft mode » whose existence correlates with the structural transition. Existing theories of « soft modes » are to varying degrees phenomenological, in the context of lattice dynamics, and our proposal is an attempt to go beyond this phenomenology. Thus, in this model, we must determine the participating, unstable, electronic state. In the cases at hand, this leads us rather directly to the par-

tially filled, « resonating », hybridized valence bonds we use, since the pure  $p$  states do not satisfy the criterion for instability. While the use of valence-bond concepts has heretofore largely been restricted to a subset of « theoretical chemists », recently the ideas of valence bonds have been taken up in solid state physics [27]. Naturally, the only validation of these concepts will be via quantitative agreement between theoretically calculated quantities and experimental measurements of the same observables.

The validity of the thermodynamic theory of second order phase transitions in crystals, and of its application to the present case, is quite a separate matter. The results obtained here on permissible symmetry changes from rocksalt structure are generally valid as long as the thermodynamic theory applies. There is good reason to believe that existing criteria [28] for validity of this theory support its use in the present case, irrespective of the microscopic dynamical model put forth.

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- [17] BACHER (R. F.), GOUDSMIT (S.), *Atomic Energy State* (McGraw-Hill, N. Y., 1932).
- [18] ALTMAN (S.), COULSON (C. A.), HUME-ROTHERY (W.), *Proc. Roy. Soc.*, 1957, **A240**, 145.
- [19] BIRMAN (J. L.), *J. Chem. Phys.*, 1963, **39**, 3147.
- [20] In réf. 19, the more general case  $\alpha \neq 0$  was developed: this leads to two non-degenerate and two doubly degenerate levels. Continuing the *post-hoc* reasoning characterizing this Section,  $\alpha = 0$  leads to predicted distortions which agree with those observed, assuming correctness of the model.
- [21] This is discussed in KIMBALL (G. E.) and HULTGREEN (R.), *loc. cit.* in ref. 16. Also BIRMAN (J. L.) (unpublished).
- [22] In KIMBALL (G. E.), *loc. cit.* ref. [16], Fig. 1, it is shown that bond angles less than  $90^\circ$  can also be achieved by a variety of  $s$ - $p$ - $d$  combinations, all of which involve at least  $1/3$  admixture of  $d$  orbitals. Hence our discussion is somewhat oversimplified, but the important point is participation of  $d$  states, relative to  $s$  states in the bonding. Again, using *post-hoc* reasoning the participation of  $d$  states in rhombohedral is at the expense of states in the bond.
- [23] For a review of Jahn-Teller effects in Solids see STURGE (M. D.) in « *Solid State Physics* » **20** (ed. SEITZ (F.), TURNBULL (D.), EHRENREICH (H.)), Academic Press, N. Y., 1967.

- [24] PAULING (L.), ref. [15], Chap. III. In the language of this author, the 10 electrons could either completely fill 5 of the 6 bonds (one pair per bond) leaving one empty bond, or 4 bonds could be filled, with one unpaired electron in each of the two remaining ones. The latter would give paramagnetism owing to unpaired spins. The actual situation reflects that configuration-mixing of these possibilities giving the lowest energy.
- [25] An example of this kind of work is given in CLOGSTON (A. M.), GOSSARD (A. C.), JACCARINO (V.), YAFET (Y.), *Rev. Mod. Phys.*, 1964, **36**, 170, where the  $V_3Si$ , and related  $\beta$ -W structures were studied. Also see GOSSARD (A. C.), *Phys. Rev.*, 1966, **149**, 246.
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## DISCUSSION

HULIN, M. — Through some Wannier-type transformations, a Bloch state and a chemical bond description can be made equivalent. How can they lead to different results concerning the possible occurrence of an irreversible lattice distortion ?

BIRMAN. — Some of these points are discussed in N. N. Kristofel', *Sov. Phys. Sol. Stat.*, 1965, **6**, 2613.

**Note added in proof.** — The discussion in the text (paragraph 4) is put in the localized bond framework for reasons of simplicity of carrying out the argument. Of course, you are correct, that the two descriptions can be made equivalent. But to use the BLOCH state framework would, I believe, require summing up contributions to the « instability integral » from all over the Brillouin zone. It seems that the argument I gave in text is more direct.