Functional Crystals: Search Criteria and Design Principles

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Conceptually, there are three levels of design strategy for functional crystals. The first level is the point group symmetry. In fact, point-group symmetry dictates the presence or absence of a particular physical response (and its anisotropy) of a crystal; hence, it can be used to search and/or screen for new functional crystals. The symmetry requirements of a number of technologically important physical properties of functional crystals are described. However, point-group symmetry is a necessary requirement but not a sufficient condition for a functional crystal. For a crystal to exhibit a particular property, it must be augmented by the second level of design strategy—the structure pattern or the space-group symmetry. Finally, in order to enhance or optimize the response, the third level of design strategy, molecular engineering, which involves the fine tuning of the electronic or magnetic structures of the building blocks (atoms, molecules, clusters, etc.) of the crystal, must be considered. This three-level strategy for designing functional crystals is discussed with the aid of examples from a new class of hybrid crystalline materials based on inorganic polymers with organic spacers/controllers systems recently developed by us. © 2000 Academic Press

Key Words: functional crystals, design strategies; structural patterns; molecular and crystal engineering; hybrid materials; symmetry requirements; inorganic polymers with organic spacers.

I. INTRODUCTION

The past decade had seen an exponential growth in many areas of science and technology. Such explosive growth is made possible by advances in, and the synergism between, various disciplines of modern science and technology. No doubt we are at the dawn of digital, optical, molecular, and biological revolutions, to name just a few (1–3). These revolutions are driven by the ever-increasing demand for powerful and smart devices, both in commercial and defense applications.

The foundation of these revolutions is materials technology. In fact, the design, synthesis, and growth of functional materials are prerequisites to the fabrication and manufacture of technologically important devices such as piezoelectric transducers and optical frequency converters for lasers

(4–8). A functional material may be defined as a material that performs a particular function (output) upon receiving a particular stimulus (input) where the input and output signals may be physical, chemical, or biological. A functional crystal, in particular, may be defined as a crystal which exhibits a particular physical property (for example, mechanical, thermal, optical, electrical, or magnetic properties) upon excitation by an external stimulus.

Examples of functional materials include inorganic, organic, and polymeric materials as well as liquid crystals, composites, etc. (4–8). Inorganic crystals such as lithium niobate are dominant technological materials for decades and are still the state-of-the-art crystals widely used in nonlinear optical applications, electro-optic devices, integrated optics, etc. (9). These crystals exhibit superior electro-optical, piezoelectrical, and photorefractive properties and have the advantages of good stability, high mechanical strength, multifunctionality, etc. The drawbacks of inorganic crystals include difficulties in crystal growth and in integration with electronic devices, etc. These difficulties render their applications more difficult in many applications than that seen in the rapidly emerging organic or polymeric film technologies (5). While the organic-based materials are more amenable to derivatization, modification, and fabrication, they suffer from low damage threshold, poor mechanical, thermal, and light stabilities, etc.

In order to take advantage of the superior qualities of both inorganic, organic, and polymer materials, we have recently developed a new class of hybrid crystal materials based on inorganic polymers with organic spacers/controllers (IPOS) systems (10–12). For example, we have designed, synthesized, and structurally characterized a new series of hybrid crystalline materials consisting of cationic crown–ether metal complexes and the anionic cadmium-thiocyanate polymers. These coordination solids form a wide variety of structures, ranging from one-dimensional (1D) chain structures (as exemplified by $[(18C6)K]\,[Cd(SCN)_3]$ (**1**) (10a) and $[(18C6)_2Na_2(H_2O)_2]\,[Cd(SCN)_3]$ (**2**) (10a) to two-dimensional (2D) layered structures (as observed in $[(12C4)_2Cd]\,[Cd_2(SCN)_6]$ (**11a**) and $[(12C4)_2Cd]\,[Cd_3(SCN)_8]$ (**11b**), depending upon the size, shape, symmetry, and charge of the cationic host–guest complexes. In this

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regard, the cations serve as the spacers, controllers, and, in some cases, templates, dictating the crystal symmetry and structure, and, ultimately, the physical properties of the crystals.

Generally speaking, symmetry plays a central role in characterizing the physical properties of the crystals. For example, in a crystal, the absence of a center of symmetry is an essential requirement for many important physical properties such as pyroelectricity, ferroelectricity, piezoelectricity, second-order nonlinear optical property, electro-optical property, and photorefractivity. Table 1 summarizes the symmetry requirements of some important physical properties of functional crystals. In this review, we shall, based on symmetry considerations, provide an account of the search criteria and design principles for functional crystals, using the above-mentioned IPOS system as examples. It should be pointed out, however, that the general strategies and structural principles described herein are applicable to other functional crystals as well, including inorganic, organic, polymeric, hybrid, and composite materials.

II. FROM FUNCTIONAL TO SMART TO INTELLIGENT SYSTEMS

Functional materials are the "bricks" and "mortars" of the so-called "smart" or "intelligent" systems. They are, in fact, the materials that constitute the components or building blocks of these systems. As depicted schematically in Chart 1, a "smart structure," with its sensors (input) and actuators (output) and the central processing unit (CPU), has the capacity to sense its environment and react in a defined and predictable manner. With the addition of an artificial neural network (ANN) to such a system, one creates an "intelligent system" which has the ability to learn, adapt, and optimize its responses, in real time, to external stimuli or environment (13).

One smart structure that is currently being used in many applications is the piezoelectric device, capable of detecting excessive vibration and responding by applying an opposing current to counteract and dampen the vibration. Piezoelectric devices are either crystals, ceramics, or polymeric films that act as electromechanical transducers. They

TABLE 1
Symmetry Requirements of Functional Crystals with Interesting Physical Properties under the Seven Crystal Systems[a]

Crystal system	Noncentrosymmetric point groups[b]	Physical properties[b]					Centrosymmetric point groups[c]
		Pyroelectricity	Ferroelectricity	Piezoelectricity	Second-order nonlinear optical properties	Linear electrooptics	
Triclinic	C_1—1	X	X	X	X	X	C_i— −1
Monoclinic	C_2—2	X	X	X	X	X	C_{2h}—2/m
	C_s—m	X	X	X	X	X	
Orthorhombic	D_2—222	0	0	X	X	X	D_{2h}—mmm
	C_{2v}—mm2	X	X	X	X	X	
Tetragonal	C_4—4	X	X	X	X	X	C_{4h}—4/m
	S_4— −4	0	0	X	X	X	D_{4h}—4/mmm
	D_4—422	0	0	X	0	X	
	C_{4v}—4mm	X	X	X	X	X	
	D_{2d}— −42m	0	0	X	X	X	
Trigonal	C_3—3	X	X	X	X	X	S_6— −3
	D_3—32	0	0	X	X	X	D_{3d}— −3m
	C_{3v}—3m	X	X	X	X	X	
Hexagonal	C_6—6	X	X	X	X	X	C_{6h}—6/m
	C_{3h}— −6	0	0	X	X	X	D_{6h}—6/mmm
	D_6—622	0	0	X	0	X	
	C_{6v}—6mm	X	X	X	X	X	
	D_{3h}— −62m	0	0	X	X	X	
Cubic	T—23	0	0	X	X	X	T_h—m3
	O—432	0	0	0	0	0	O_h—m3m
	T_d— −43m	0	0	X	X	X	
Total	21	10	10	20	18	20	11

[a] Point groups are specified by Schoenflies symbols followed by Hermann–Mauguin designations.

[b] Noncentrosymmetric point groups capable of exhibiting the physical properties listed here are indicated by Xs while those incapable are designated by 0s.

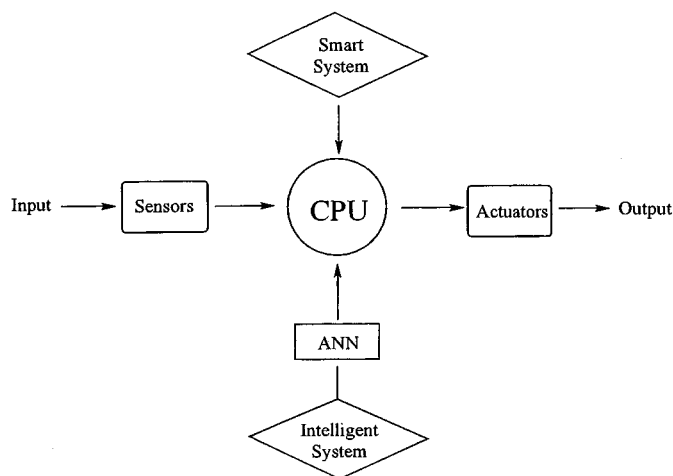[c] All centrosymmetric point groups exhibit none of the physical properties listed here.

CHART 1. Functional materials as components or building blocks for smart or intelligent systems (see text).

knowledge, only two kinds of infinite $[Cd(SCN)_3^-]_\infty$ polymers. These two types, hereafter referred to as A and B, are portrayed in Figs. 1a and 1b, respectively. An important stereochemical difference between the two types of $[Cd(SCN)_3^-]_\infty$ chains listed in Table 2 is that type A $[Cd(SCN)_3^-]_\infty$ polymers have zig-zag cadmium chains with average $Cd \cdots Cd \cdots Cd$ angles of 165° (see Fig. 2a for $[(18C6)K][Cd(SCN)_3]$ (**1**) (10a) as an example) while the cadmium chains in type B $[Cd(SCN)_3^-]_\infty$ polymers are essentially linear with $Cd \cdots Cd \cdots Cd$ angles of 179.8° (see Fig. 2b for $[(DB24C8)Na][Cd(SCN)_3]$ (**6**) (10d) as an example). This difference has a profound influence on the relative alignment of the chains in the crystal structure, thereby impacting on their physical properties. Furthermore, the spatial arrangement and the relative alignment of the zig-zag $[Cd(XCN)_3^-]_\infty$ chains can be controlled and/or induced by the cations (to be discussed next).

(1) Point-Group Symmetry

The first level of design strategy is point-group symmetry. In fact, point-group symmetry dictates the presence or absence of a particular physical response of a crystal. For example, crystals with an inversion center cannot possess properties such as pyroelectricity, piezoelectricity, and second-order nonlinear optical properties. In other words, for these properties, it is important to design and fabricate crystals with noncentrosymmetric symmetries. Point-group symmetry requirements of functional crystals with
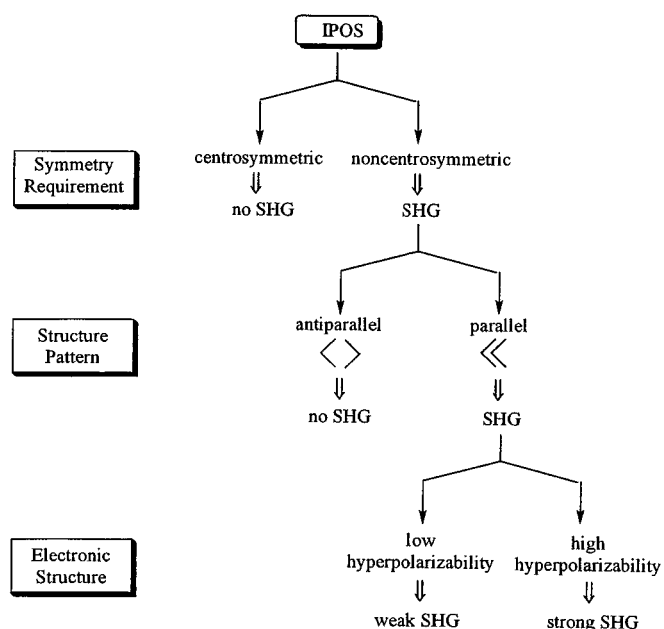
are capable of converting an electrical signal into mechanical motion, and vice versa. In some applications, piezoelectrical devices can both sense changes in a structure and send an electrical signal to effect a change in the structure, thereby providing instant, real-time response to, for example, a mechanical stress (14).

In short, functional materials are the building materials for smart systems that can sense and respond to the environment. Furthermore, smart structures can be made into intelligent systems which can learn and adapt to the changing environment. The next decade will see intelligent systems enhancing, replacing, or even competing with many human functions.

III. FUNCTIONAL CRYSTALS: THREE LEVELS OF DESIGN STRATEGY

In our view, there are, conceptually, three levels of design strategy for functional crystals. We shall use examples from our recent studies of the nonlinear optical crystals based on the IPOS systems (10–12) to illustrate the hierarchy of the three levels of design strategy, as illustrated schematically in Chart 2. The design, syntheses, crystal structures, and properties of these highly interesting low-dimensional IPOS coordination solids have been reviewed by us in the literature (12). In this paper, we shall focus our attention on the crystal and molecular structures of 1D IPOS coordination solids of general formula [cation] $[Cd(XCN)_3]$ where $X = S$, Se, Te and cation = host–guest complexes, R_4N^+ (R = alkyl, aryl groups), etc.

Despite the versatility of the 1–D $[Cd(SCN)_3^-]_\infty$ chains in crystallizing in a variety of crystal systems and space groups, resulting in different types of channels and relative alignments of the chains (see Table 2), there are, to the best of our

CHART 2. Three levels of design strategy for 1D IPOS systems for second-order nonlinear optical (SHG) effects (see text).

No.	Cation	Space group	Channel	Alignment
1	[(18C6)K]$^+$	$Cmc2_1$	◇	⟨⟨
2	[(18C6)$_2$Na$_2$(H$_2$O)$_2$]$^{2+}$	$P2_1/n$	◇	⟨⟩
3	[(12C4)Na]$^+$	$P2_1/n$	△	⟨⟩
4	[Et$_4$N]$^+$	$Cmc2_1$	△	⟨⟨
5	[Me$_4$N]$^+$	$Pna2_1$	△	⟨⟩
6	[(DB24C8)Na]$^+$	Cc	△	‖

technologically important physical properties are tabulated in Table 1.

Using the 1D IPOS series as an example, for second-order nonlinear optical effects such as second harmonic generation (SHG), it is important to choose cations which lack the inversion symmetry or are less prone to reside on an inversion center, or are in itself less symmetrical or spherical in shape. Figure 3 illustrates the size and shape of the

Type A   Type B

FIG. 1. Two types of the infinite anionic [Cd(SCN)$_3^-$]$_\infty$ chains, type A and type B, as exemplified by (a) [(18C6)K][Cd(SCN)$_3$] (1) and (b) [(DB24C8)Na][Cd(SCN)$_3$] (6), respectively. Note that type A has crystallographic 2_{1c}, m_a, and c_b intrachain symmetries, whereas type B has only c_b symmetry.

commonly observed crown–either alkali-metal complexes as cations which have been used extensively in our study (10–12, 15). In order to enhance the tendency of forming noncentrosymmetric space groups, the monomeric host–guest (1 : 1) complexes of a disk-like, a partially coiled, or a coiled structure, as portrayed in Figs. 3a–3c, respectively, should be used as cationic spacers/controllers. To prevent the formation of centric space groups, symmetrical cationic host–guest molecules such as dimeric structures (Figs. 3d and 3e), sandwich complexes (Fig. 3f) or two-nuclei complexes (Fig. 3g) should be avoided as these latter complexes are symmetrical in shape or tend to reside on the inversion center, thereby increasing the tendency for the formation of centrosymmetric crystal structures. Two representative examples (10a) are [(18C6)K][Cd(SCN)$_3$] (1) and [(18C6)$_2$Na$_2$(H$_2$O)$_2$][Cd(SCN)$_3$] (2). The disk-like cation [(18C6)K]$^+$ in 1 and the dimeric structure of the dication [(18C6)$_2$Na$_2$(H$_2$O)$_2$]$^{2+}$ in 2 result in crystallization in noncentrosymmetric ($mm2$) for 1 and centrosymmetric ($2/m$) for 2, respectively. It should be mentioned that noncentrosymmetric space groups for the IPOS crystals generally give rise to a parallel alignment of the zig-zag [Cd(SCN)$_3^-$]$_\infty$ chains (see Fig. 4, left), as observed in 1. The centrosymmetric space groups, on the other hand, results in an antiparallel alignment of the zig-zag chains, as illustrated in Fig. 4 (right), for 2. Consequently, the former (1) exhibits efficient second-order nonlinear optical responses while the latter (2) does not (10a).

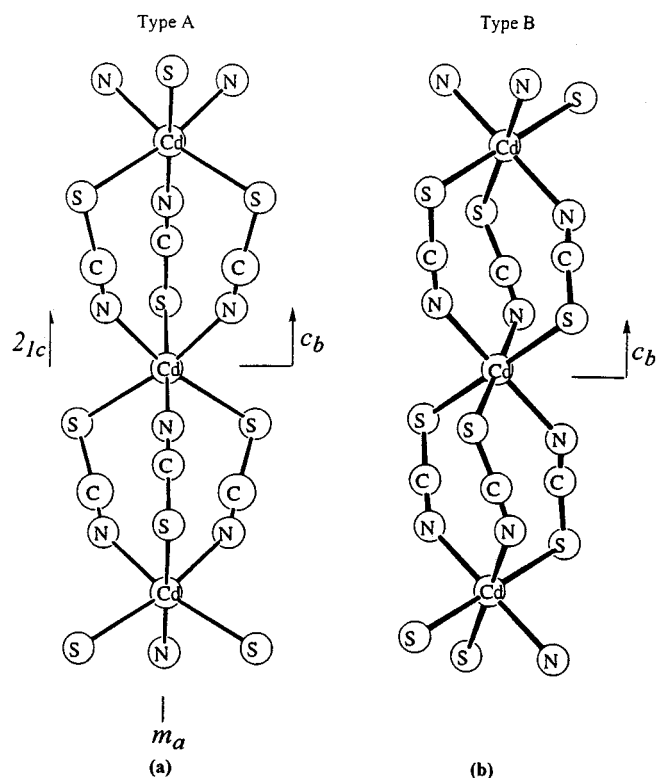## (2) Structure Pattern (Space-Group Symmetry)

The second level of design strategy is the structural pattern of a crystal. Implicitly, the structure pattern of a crystal manifests itself in the space-group symmetry. Conversely, space-group symmetry determines the structural pattern of a crystal, which, in turn, dictates its physical properties. Depending upon how atoms (or ions) or molecules are arranged in a crystal, they may help to enhance, diminish, or even completely nullify a particular physical response. For
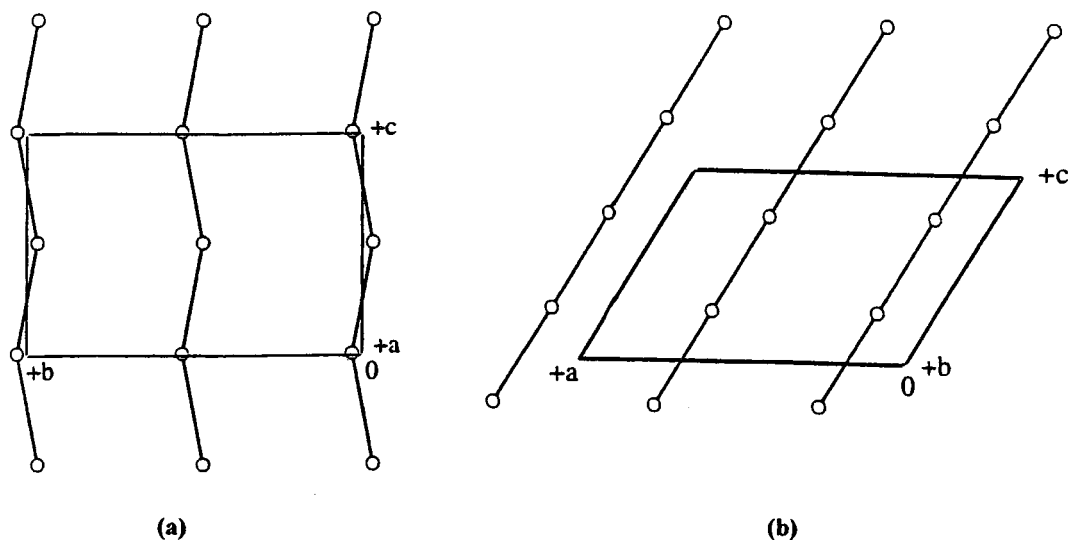
FIG. 2. (a) Parallel alignment of zig-zag cadmiuim chains (type A) as observed in [(18C6)K][Cd(SCN)$_3$] (**1**) (10a). (b) Parallel alignment of linear cadmium chains (type B) as observed in [(DB24C8)Na][Cd(SCN)$_3$] (**6**) (10d).

example, as tabulated in Table 2, it is apparent that, in space group $Cmc2_1$ (as observed for **1** and **4**), the neighboring zig-zag [Cd(SCN)$_3$]$^-_\infty$ chains (type A) are related by C-
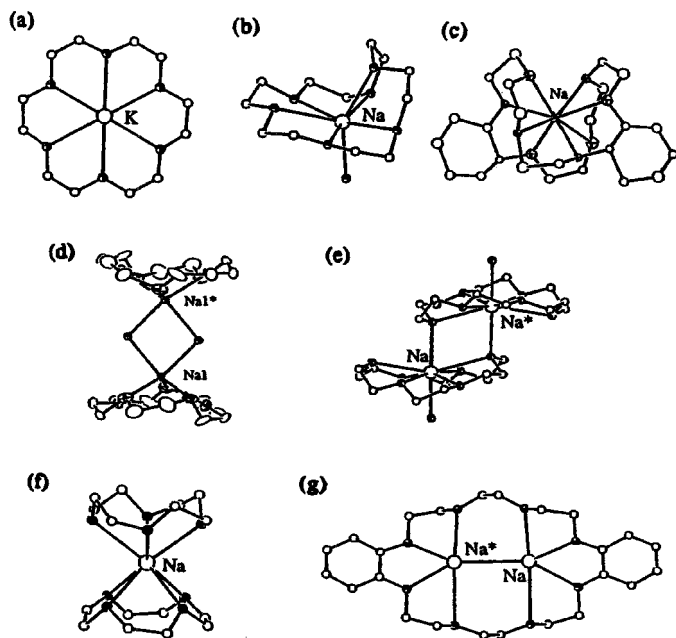

FIG. 3. Representative examples of seven categories of the commoly observed crown-ether (host) alkali-metal (guest) structures (10–12, 15): (a) disk-like (host:guest = 1:1) as in [(18C6)K][Cd(SCN)$_3$] (**1**) (10a); (b) partially coiled (1:1) as in [(18C6)Na(H$_2$O)][(SCN)]; (c) coiled (1:1) as in [(dibenzo-24C8)Na][Cd(SCN)$_3$] as in [(DB24C8)Na][Cd(SCN)$_3$] (**6**) (10d); (d) dimer (2:2) as in [(15C5)$_2$Na$_2$(H$_2$O)$_2$]$_{1/2}$[Cd$_2$(SCN)$_5$] (11c); (e) dimer (2:2) as in [(18C6)$_2$Na$_2$(H$_2$O)$_2$]$_{1/2}$[Cd(SCN)$_3$] (**2**) (10a); (f) sandwich (2:1) as in [(12C4)$_2$Na][Cd(SCN)$_3$] (10b); and (g) two nuclei (1:2) as in [(dibenzo24C8)Na$_2$][o-O$_2$NC$_6$H$_4$O]$_2$.

centering (as well as screw axis 2_{1c} and two glide planes, b_a and n_b). The implication of this interchain crystallographic symmetry is obvious: the adjacent zig-zag chains must be aligned parallel to one another (see Fig. 4a for **1**). In fact, the parallel alignment gives rise to SHG (10a). In contrast, the adjacent chains in **2** and **3** (space group $P2_1/n$) are related by the inversion center (-1), as well as glide plane n_b, making their relative alignment antiparallel (see Fig. 4b for **2**), and thus nullifying the SHG response. Finally, let us compare the two tetraalkylammonium salts, [Et$_4$N][Cd(SCN)$_3$] (**4**) and [Me$_4$N][Cd(SCN)$_3$] (**5**), listed in Table 2. We note that, in contrast to the arrangement in **4**, the adjacent (type A) chains in **5** are related by 2_{1c} and n_a. The lack of inversion symmetry in the crystal structure of **5** initially suggested that the neighboring chains might be aligned in a parallel fashion. Optical measurements, however, exhibited weak or no SHG response for **5**. A subsequent examination of the crystal structure of **5** revealed that the zig-zag chains are aligned in an approximately antiparallel manner, which explains the lack of the SHG response (10c). The antiparallel alignment in **5** was rationalized in terms of the small size of (Me$_4$N)$^+$ cations which are nested in the "pockets" formed by the zig-zag [Cd(SCN)$_3$]$^-_\infty$ chains.

As indicated in Table 2, the adjacent [Cd(SCN)$_3$]$^-_\infty$ chains in **6** are related by the crystallographic C-centering which implies that they must be aligned in a parallel fashion. Unfortunately, as discussed earlier, the type B chains in **6** have essentially linear Cd $\cdots$ Cd $\cdots$ Cd chains (see Fig. 2b) which makes the distinction between parallel and antiparallel a moot point. This is one of the reasons (others to be discussed in the following section) that **6** exhibits weak or no SHG effects (10d).
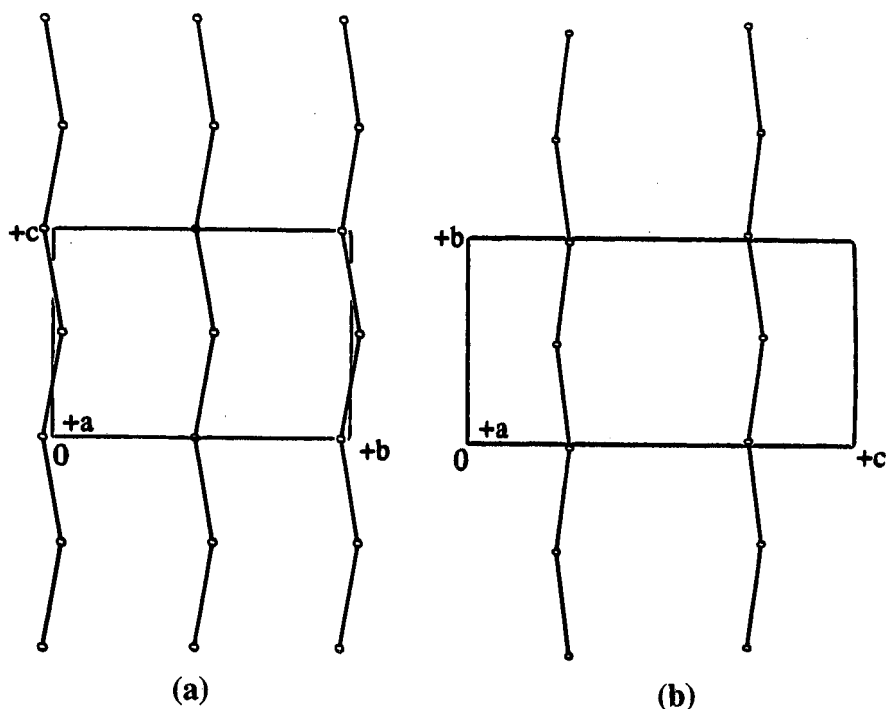
FIG. 4. The Cd atoms in $[(18C6)K][Cd(SCN)_3]$ (**1**) and $[(18C6)_2Na_2(H_2O)_2]_{1/2}[Cd(SCN)_3]$ (**2**) form infinite zig-zag chains with Cd$\cdots$Cd distances of 5.41 Å and Cd$\cdots$Cd$\cdots$Cd angles of 162° and with (a) parallel alignment in **1** and (b) antiparallel alignment in **2** (10a).

In short, for the parallel alignment, dipole moments from the individual chains add up to produce a net dipole moment for the crystal that is a prerequisite for the macroscopic second-order nonlinear optical properties. The antiparallel alignment results in the cancellation of the dipole moments from individual chains and the nullification of the net dipole moment for the crystal and hence no second-order nonlinear optical responses.

(3) Optimization of Physical Responses

The third level of design strategy is the optimization of the responses. This may involve fine tuning electronic or magnetic properties of the atoms, molecules, or other cluster building blocks constituting the crystal. For instance, in order to maximize nonlinear optical properties, atoms with high degree of electron polarizability or molecules with a large change in dipole moments between ground and excited states should be chosen. Using the IPOS system as an example, it was observed that $[Et_4N][Cd(SeCN)_3]$ (**7**) is a better second harmonic crystal than $[Et_4N][Cd(SCN)_3]$ (**4**) due to the higher polarizability of the selenocyanate ligands (in comparison with the thiocyanide ligands) (10c). It is anticipated that, in going from $[Cd(SCN)_3^-]_\infty$ to $[Cd(SeCN)_3^-]_\infty$ to $[Cd(TeCN)_3^-]_\infty$, the nonlinear optical properties should increase significantly. Furthermore, **7** was

found to be phase matchable, while the homologous **4** was not. This latter effect is rather subtle and deserves further scrutiny, from both experimental and theoretical viewpoints.

Another strategy in enhancing second-order nonlinear optical responses is to employ an asymmetric ligand arrangement in the metal coordination sphere which will lead to high asymmetric electronic distribution around the metal atom. In this context, we note that there are two types of isomers for an octahedral MA_3B_3 coordination complex —*fac* and *mer*—as shown in Fig. 5 for CdN_3S_3. It turns out that type A $[Cd(SCN)_3^-]_\infty$ chains adopt the *fac*-CdN_3S_3 coordination, whereas type B $[Cd(SCN)_3^-]_\infty$ chains exhibit the *mer*-CdN_3S_3 configuration (cf. Fig. 1). The *fac*-CdN_3S_3 and *mer*-CdN_3S_3 configurations are related by a relative rotation of 120° of the two triangles (comprising S, S, N and N, N, S) about the chain axis, as illustrated schematically in Fig. 5. With the *fac*-CdS_3N_3 configuration, the S atoms are *trans* to the N atoms, giving rise to asymmetric electronic distribution around the Cd atoms. This asymmetric electron density distribution is highly desirable in the optimization of the second-order NLO effects. With the *mer*-CdS_3N_3 configuration, on the other hand, two pairs of like atoms are *trans* to one another (S to S and N to N), leaving only one unlike atom pair being *trans* to each other (S to N). This implies that the asymmetry of electron density distribution around the Cd atom with the *mer*-CdN_3S_3
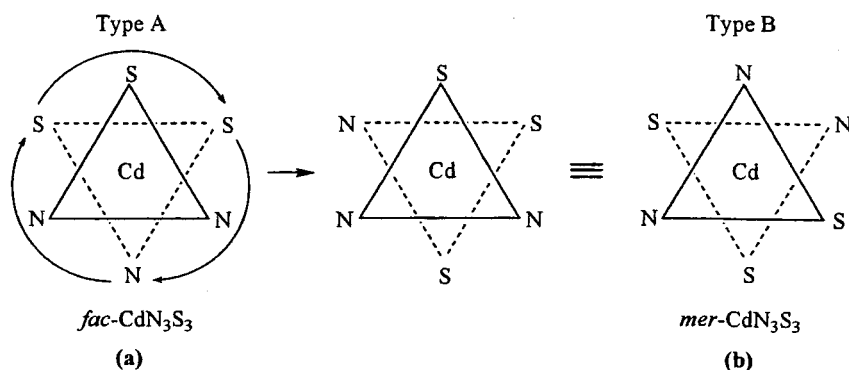
FIG. 5. Interrelationship between *fac-* and *mer-*CdN$_3$S$_3$ coordination spheres. A 120° rotation of the bottom SSN triangle of *fac-*CdN$_3$S$_3$ (a) about the chain axis gives rise to *mer-*CdN$_3$S$_3$ (b) (10d).

configuration is greatly reduced in comparison with that in *fac-*CdS$_3$N$_3$ configuration. This consideration led to the prediction that, at the level of molecular engineering, the second-order NLO responses for type B structures with the *mer-*CdS$_3$N$_3$ configuration, if any, should be significantly less than that for the type A structures with the *fac-*CdS$_3$N$_3$ coordination, as was indeed observed (10d).

IV. ADVANTAGEOUS PROPERTIES OF THE ONE-DIMENSIONAL (1D) IPOS SYSTEM

The beneficial properties or characteristics of this class of IPOS coordination solids are as follows (10–12). First, the anionic $[Cd(XCN)_3^-]_\infty$ chains (where X = S, Se, Te) form isolated (well separated) polymeric structures of low dimensionality (e.g., 1D or 2D), giving rise to anisotropic physical properties. Second, the extended π-conjugation system within the polymeric cadmium-chalcogenocyanate, with the high polarizabilities of both the metal and the ligand, gives rise to desirable physical properties such as NLO effects. Third, the cations serve as spacers/controllers of the crystal structure and crystal symmetry. For second-order nonlinear optical effects such as second harmonics generation (SHG), it is important to arrange the zig-zag cadmium-thiocyanate chains in a parallel fashion, as exemplified by **1** and **4**. Antiparallel alignment of the zig-zag cadmium-thiocyanate chains will effectively nullify any second-order NLO effects, as seen in **2**, **3**, and **5**. Even if the crystal adopts a structure with a noncentrosymmetric space group, antiparallel alignment of the zig-zag chains may sometimes be observed, as in **5**. Fourth, these coordination solids show typical properties of ionic compounds such as relatively high melting points and good mechanical properties. Fifth, the ability to fine tune the molecular parameters (e.g., from S to Se to Te, from Me$_4$N$^+$ to Et$_4$N$^+$, and from *fac-* to *mer-*CdN$_3$S$_3$ coordination) and the crystal structures (e.g., from space group *Pna*2$_1$ to *Cmc*2$_1$, from linear to zig-zag Cd chains, and from parallel to antiparallel alignments of the zig-zag chains) opens the door to tailorable crystals with desirable physical properties. Finally, and perhaps most importantly, the IPOS coordination solids based on combination of d^{10} metal such as Cd(II) and XCN$^-$ ligands (where X = chalcogenide series) have the added advantage of being optically transparent from near ultraviolet (220 nm) to near infrared (3300 nm) regions (i.e., a very wide and continuous optical window), making it useful for a broadband frequency conversion applications (10–12).

V. CONCLUSION

In conclusion, there are, in our view, three levels of design strategy for functional crystals. At the first level, point-group symmetry plays a pivotal role in dictating whether or not a crystal can exhibit a particular physical property (see Table 1 for examples). In a word: symmetry "rules." This first level of the design strategy, however, can only serve as a screening tool in the search of new functional crystals. In many instances, point-group symmetry is a *necessary* requirement but *not a sufficient* condition for a functional crystal. For a crystal to exhibit a particular property, it must be augmented by the second level of the design strategy, the structure pattern, which is governed by the space-group symmetry. Thus, these two levels of design strategy (i.e., point-group and space-group symmetries) may be regarded as crystal engineering. Finally, in order to enhance or optimize the response, the third level of design strategy—molecular engineering—must be considered. Molecular engineering involves fine tuning the electronic or magnetic structures of building blocks (atoms, molecules, clusters, etc.) of the crystal to enhance the desirable properties. Work is in progress, both experimentally and theoretically, to further these ideas.

REFERENCES

1. (a) P. K. Das, "Optical Signal Processing," Springer-Verlag, New York, 1990; (b) J. Jahns, *Optik* **57,** 429 (1980); (c) R. D. Guenther, "Modern Optics," Wiley, New York, 1990; (d) B. E. A. Saleh and M. C. Teich, "Fundamentals of Photonics," Wiley, New York, 1991. (e) H. M. Gibbs, *Laser Focus* 21 (1985); (f) P. Batacan, *Comput. Phys.* **2,** 9 (1988).

2. (a) F. Zernike and J. E. Midwinter, "Applied Nonlinear Optics," Wiley, New York, 1973; (b) S. Singh *in* "Handbook of Laser Science and Technology" (R. J. Pressley, Ed.), part 2, p. 3, CRC Press, Boca Raton, FL, 1971; (c) C. Flytzanis and J. L. Oudar, "Nonlinear Optics Materials and Devices," Springer, New York, 1986; (d) J. Zyss, *J. Mol. Electron.* **1,** 25 (1985).

3. (a) A. M. Glass, *MRS Bull.* **13,** 16 (1988); (b) Y. X. Fan, R. C. Eckhardt, R. L. Byer, R. K. Route, and R. S. Fiegelson, *Appl. Phys. Lett.* **45,** 313 (1984).

4. (a) R. C. Miller, D. A. Kleinman, and A. Savage, *Phys. Rev. Lett.* **11,** 146 (1963); (b) R. C. Miller, G. D. Boyd, and A. Savage, *Appl. Phys. Lett.* **6,** 77 (1965); (c) C. Chen and G. Liu, *Annu. Rev. Mater. Sci.* **16,** 203 (1986).

5. (a) "Nonlinear Optical Properties of Organic and Polymeric Materials" (D. J. Williams, Ed.), ACS Symp. Ser. 233, American Chemical Society, Washington, D. C. 1983; (b) "Materials for Nonlinear Optics: Chemical Perspectives," (S. R. Marder, J. E. Sohn, and G. D. Stucky, Eds.), *ACS Symp. Ser.* 455, American Chemical Society, Washington, DC, 1991.

6. (a) D. R. Kanis, M. A. Ratner, and T. J. Marks, *J. Am. Chem. Soc.* **114,** 10338 (1992); (b) G. R. Meredith, *Opt. Commun.* **39,** 89 (1981); (b) S. D. Cox, T. E. Gier, G. D. Stucky, and J. Bierlein, *J. Am. Chem. Soc.* **110,** 2986 (1988); (c) F. Kajzar, J. Messier, *Phys. Rev. A* **32,** 2352 (1985).

7. L.-T. Cheng, W. Tam, S. H. Stevenson, and G. R. Meredith, *J. Chem. Phys.* **95,** 10631 (1991); (b) F. Meyers, J. L. Bredas, and J. Zyss, *J. Am. Chem. Soc.* **114,** 2914 (1992); (c) A. E. Stiegman, E. Graham, K. J. Perry, L. R. Khundkar, S.-T. Cheng, and J. W. Perry, *J. Am. Chem. Soc.* **113,** 7658 (1991).

8. (a) G. D. Boyd, E. Buehler, F. G. Storz, and J. H. Wernick, *IEEE J. Quant. Electron* **8,** 419 (1972); (b) J. J. Wynne, *Phys. Rev. Lett.* **27,** 17 (1971); (c) M. Knut and T. Lindahlim, *Acta Crystallogr. A* **53,** 366 (1997).

9. (a) K. Chah, and M. D. Fontana, *Appl. Phys. B* **67,** 65 (1998); (b) D. Kip, *Appl. Phys. B* **67,** 131 (1998).

10. (a) H. Zhang, X. Wang, and B. K. Teo, *J. Am. Chem. Soc.* **118,** 11813 (1996); (b) H. Zhang, X. Wang, K. Zhang, and B. K. Teo, *Inorg. Chem.* **37,** 3490 (1998); (c) H. Zhang, Z. Zelmon, G. Price, and B. K. Teo, *Inorg. Chem.* **39,** 1868 (2000); (d) H. Zhang, X. Wang, Z. Zelmon, and B. K. Teo, submitted for publication.

11. (a) H. Zhang, X. Wang, H. Zhu, W. Xiao, and B. K. Teo, *J. Am. Chem. Soc.* **119,** 5463 (1997); (b) H. Zhang, X. Wang, H. Zhu, W. Xiao, and B. K. Teo, *Inorg. Chem.* **38,** 886 (1999); (c) H. Zhang, X. Wang, and B. K. Teo, submitted for publication.

12. H. Zhang, X. Wang, K. Zhang and B. K. Teo, *Coord. Chem. Rev.* **183,** 157 (1999).

13. (a) A. D. McAulay, "Optical Computer Architectures," Wiley, New York, 1991. (b) B. S. Wherrett, *Comput. Phys.* **2,** 24 (1988); (c) Y. S. Abumostafa and D. Psaltis, *Sci. Am.* **256,** 88, (1987); (d) J. W. Goodman, *Proc. IEEE* **65,** 29 (1977).

14. (a) R. C. Miller and W. A. Nordland, *Phys. Rev. B* **2,** 4896 (1970); (b) R. C. Miller, S. C. Abrahams, R. L. Barns, J. L. Bernstein, and W. A. Nordland, *Solid State Commun.* **9,** 1463 (1971); (c) R. K. Chang, J. Ducuing, and N. Bloembergen, *Phys. Rev. Lett.* **15,** 415 (1965).

15. (a) C. J. Pedersen, *J. Am. Chem. Soc.* **89,** 2495, 7017 (1967); (b) J. M. Lehn, *Acc. Chem. Res.* **11,** 49 (1978); (c) D. J. Cram and J. M. Cram, *Acc. Chem. Res.* **11,** 8 (1978); (d) "Host Guest Complex Chemistry I, II, (F. Vogtle, Ed.), Topics in Current Chemistry, Vols. 98 and 101, Springer-Verlag, Berlin, 1981, 1982; (e) M. Dobler, J. D. Dunitz, and P. Seiler, *Acta Crystallogr. B* **30,** 2741 (1974); (f) M. A. Bush and M. R. Truter, *J. Chem. Soc. Perkin Trans.* **2,** 345 (1972); (g) M. Dobler and R. P. Phizackerley, *Acta Crystallogr. B* **30,** 2748 (1974); (h) D. L. Hughes, *J. Chem. Soc. Dalton Trans.* 2374 (1975).