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MSi_xGe_{2-x} Ternary Phases of the Rare Earth Metals

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The MSi_xGe_{2-x} ternary phases of the La–Dy (except Eu) metals studied fall into two main groups: (1) the La–Ce group, in which the $ThSi_2$ tetragonal structure characterizes the silicon-rich region and an orthorhombic splitting occurs in the germanium-rich region near the Si:Ge content of 1:1; and (2) the Sm–Dy group, in which the silicon-rich part is of orthorhombic structure, changing to the tetragonal phase around an Si:Ge content of 1:1. In the Pr and Nd systems almost all of the ternary phases are orthorhombic. The crystal structure of the ternary phases as well as the disilicides and digermanides is discussed.

Binary systems of rare earth metals with silicon or germanium of general composition MX_2 (M = La–Dy; X = Ge or Si) have been extensively studied. The results reported for these compounds show two main structure types: La–Pr and Eu disilicides and Pr–Sm digermanides have the $ThSi_2$ tetragonal structure[1–4] and Nd–Dy disilicides and La–Ce digermanides have the distorted orthorhombic version of the $ThSi_2$ structure.[2,3] Gd–Dy digermanides have mixed phases of the $ThSi_2$ type as well as an orthorhombic phase[5] different from the distorted $ThSi_2$. All of the digermanides reported are nonstoichiometric, with a M:Ge ratio lower than 1:2. Ternary systems with a total metal to nonmetal ratio of 1:2 have been reported for the $CeSi_xGe_{2-x}$ system[6] only.

In the present research, the MSi_xGe_{2-x} ternary phases were investigated, M being the rare earth metals La–Dy, except Eu. The aim of this study was to determine whether homogeneous solid solutions can form in these systems, the effect of the nonmetal on the crystal structure of the system, and finally a possible connection between the structure of the ternary and binary phases.

Experimental Section

Preparation of Samples.—Rare earth metals of 99.9% purity (Chemical Research Corp., Phoenix, Ariz.) and silicon and germanium metals 99.9% pure (Fluka, Buchs, Switzerland) were used. The samples were prepared by direct reaction at 1500–1700° in an induction furnace. The elements were weighed out according to their atomic ratio, mixed together, and pressed into disks, which were then placed in tantalum boats secured by tungsten wire. Each boat was inserted into a Vycor tube through which argon gas was streamed. After the air had been washed out from the tube by the argon, the samples were heated to a temperature somewhat above the melting point of the mixture and kept at this point for a few minutes.

After preparation, the compounds were checked for complete reaction and also for the presence of possible oxidation products and contamination from the reaction vessel using X-ray patterns. This method was chosen for use in conditions where chemical analysis would be certainly not more sensitive than X-ray analysis and also because it was expected— and later proved by results —that the compounds would crystallize in one of the two structures known for the lanthanide disilicides and digermanides. The results showed that no rare earth or silicon oxides were present in the compounds, probably as a result of our successful attempts at complete elimination of oxygen from the reaction site. Lines of tantalum or rare earth–tantalum compounds were also completely absent. In many cases lines of silicon, of germanium, or of their solid solution[7] appeared on the X-ray pattern of the compounds.

X-Ray Method.—Powdered samples were examined by the X-ray diffraction method, using a Philips diffractometer. The radiation used was of Ni-filtered Cu Kα (λ 1.5418 Å).

The lattice parameters were determined by least-squares refinements of 20 lines on the average. Computations were made by a least-squares refinement program[8] on an IBM 7040 computer. Good agreement was obtained between observed and calculated $\sin^2 \theta$ values. For the parameters in the order of 3.7–4.5 Å the maximum deviation was ±0.005 Å, for those in the order of 6.6–6.9 Å it was ±0.007 Å, and for those in the order of 13.3–14.2 Å it was ±0.02 Å.

Results

Examination of the X-ray diffraction patterns of the compounds studied shows that well-crystallized samples were obtained in all cases and that two types of crystal structures appear in the MSi_xGe_{2-x} systems, *viz.*, the tetragonal $ThSi_2$-type structure and its distorted orthorhombic version. The sole exceptions were the digermanides of Gd, Tb, and Dy, where, in the case of $GdGe_2$, the tetragonal structure could be detected, together with other phases, while the others gave complex patterns.

Figures 1–8 give the variation of the lattice constants *vs.* the composition of the ternary systems of La–Dy. The results obtained for the digermanides and disilicides agree well with the literature data.[1–4] The diagrams illustrating the changes in the lattice constants show clearly that transition from the tetragonal to the orthorhombic phase occurs at different compositions of the ternary phases. In Figure 9 the variation of the unit cell volume is plotted against the composition of all of the systems studied. Regular decrease of the volume can be seen in all cases of decreasing germanium content.

Figure 10 gives the results obtained for the $SmSi_x$-

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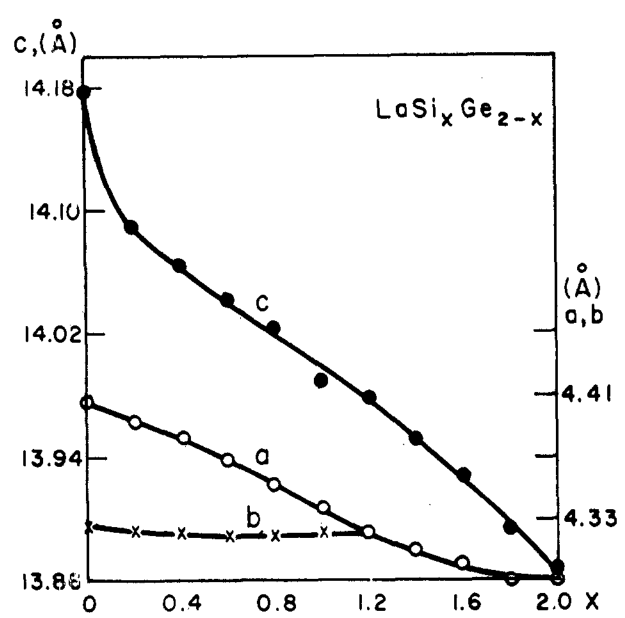

Figure 1.—Variation of lattice constants *vs.* composition of $LaSi_xGe_{2-x}$.

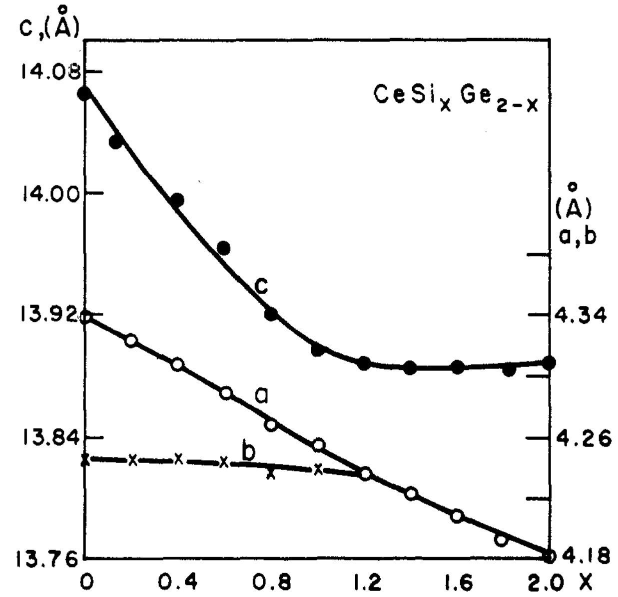

Figure 2.—Variation of lattice constants *vs.* composition of $CeSi_xGe_{2-x}$.

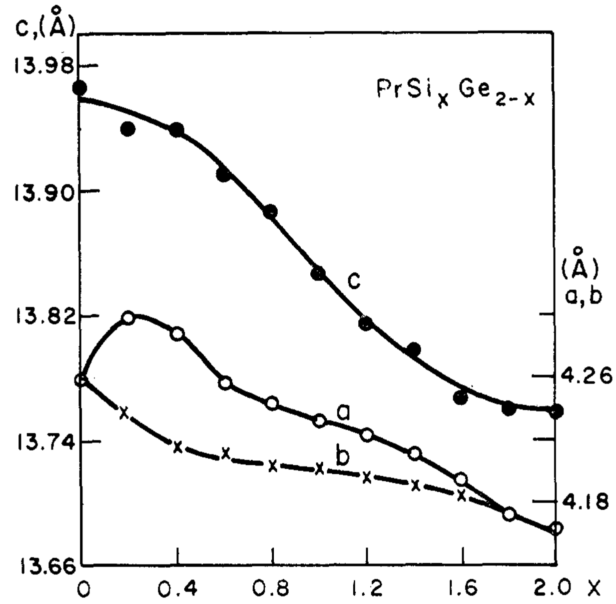

Figure 3.—Variation of lattice constants *vs.* composition of $PrSi_xGe_{2-x}$.

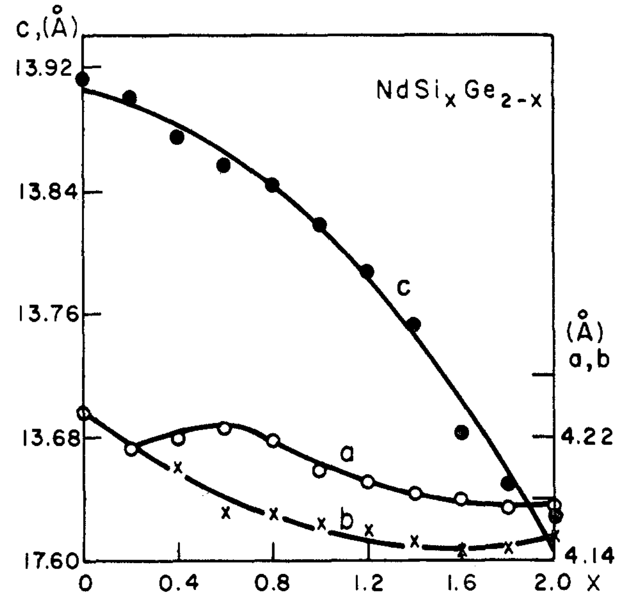

Figure 4.—Variation of lattice constants *vs.* composition of $NdSi_xGe_{2-x}$.

$Ge_{1.6-x}$ system in which the structure is a tetragonal $ThSi_2$ type.

Discussion

The crystal structure of the ternary phases investigated varies within two main groups: (1) the La–Ce group wherein the tetragonal structure characterizes the silicon-rich region and an orthorhombic splitting occurs in the germanium-rich region, the transition taking place around an Si:Ge content of 1:1; (2) the Sm–Dy group wherein the silicon-rich part is of orthorhombic structure, changing to the tetragonal phase around an Si:Ge content of 1:1. The Pr and Nd systems, where almost all of the ternary phases have the orthorhombic structure, fall between these two groups.

Changes in cell volume, on the other hand, were regular and proportional to changes in the size of atoms substituted in the various systems. Figure 11 shows the structure of the tetragonal $ThSi_2$ type of unit cell. The model is based on the space group 14_1/amd.[1] The unit cell has four molecules, four metals being in the 4b positions (z = 0.375) and eight nonmetals in the 8e positions (z = 0.786). In the orthorhombic version (space group Imma) the Si or Ge atoms are in two 4e positions with z = 0.786 and z = 0.964, the actual difference between their position in the orthorhombic as against that in the tetragonal phase being the difference in length of the a and b axes only.

Every metal atom (M) in this structure is surrounded by four nonmetals (X). The lengths of the M–3 and M–4 bonds depend on the b and c axes and those of the M–1 and M–2 bonds depend on the a and c axes. Two

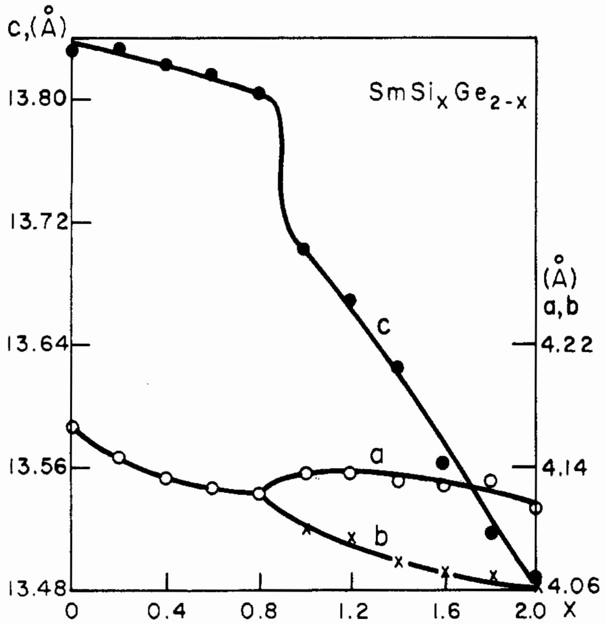

Figure 5.—Variation of lattice constants *vs.* composition of $SmSi_xGe_{2-x}$.

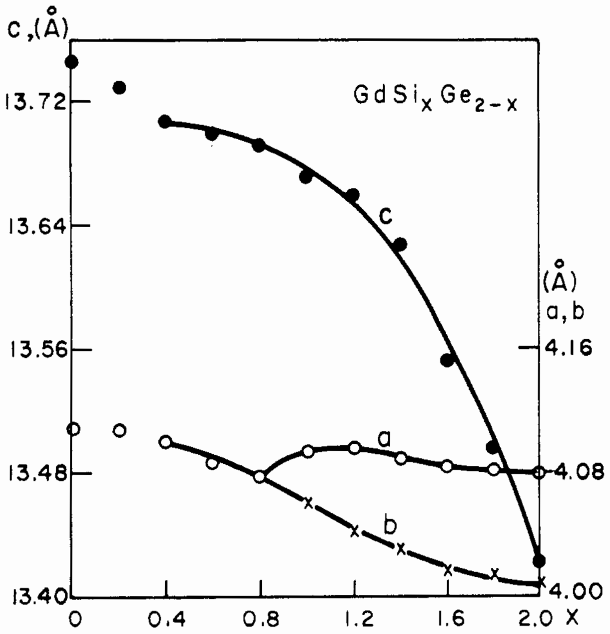

Figure 6.—Variation of lattice constants *vs.* composition of $GdSi_xGe_{2-x}$.

types of bonds exist between the nonmetals. One type forms chains, *e.g.*, atoms 5–9 (see Figure 11), the length of the chains depending on the *b* and *c* and the *a* and *c* axes, respectively. As the length of the chains depends only slightly on the *c* axis, they can be characterized as solely dependent on the *a* and *b* axes. The second type of bond between the nonmetals connects the above-mentioned chains, *e.g.*, the bonds 3–5 or 4–7, etc. The length of this bond is directly proportional to the *c* axis.

The structure of the ternary phases determined by powder diffraction data can be characterized by the distribution of the silicon and germanium atoms in the nonmetal chains and by the regular change in the cell volume. In the cases of $LaSi_xGe_{2-x}$ and $CeSi_xGe_{2-x}$, the disilicides show an intermediate *c* size. By substituting Ge for Si, germanium atoms replace silicons in the chains at random and the tetragonal structure remains. When the germanium content is in excess of 50% of the total nonmetal content, Ge–Ge bonds appear between the chains. In order to regulate the increase in cell volume, germanium atoms enter the *a*-dependent chain only, with the *a* axis increasing and *b* remaining constant. Substitution of germanium atoms in only one of the chains naturally causes orthorhombic splitting. When germanium is more than 75%, the substitution of the *b*-dependent chain begins, but the Ge atoms do not occupy all of the atomic sites available. Consequently, the changes in the lattice constants and cell volume are moderate, as was proved also by the excess of Si and Ge obtained in these phases.

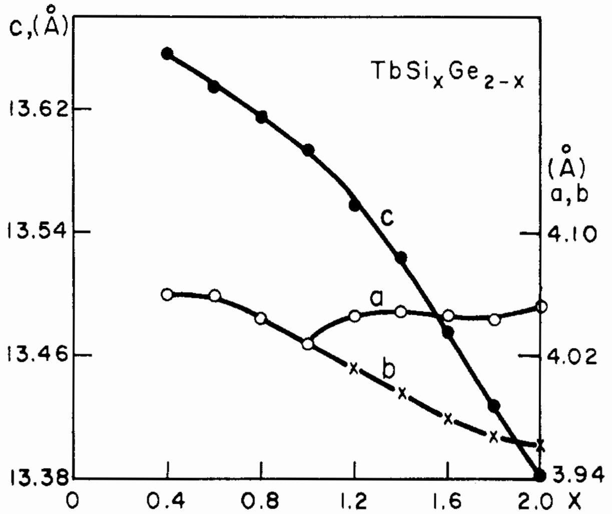

Figure 7.—Variation of lattice constants *vs.* composition of $TbSi_xGe_{2-x}$.

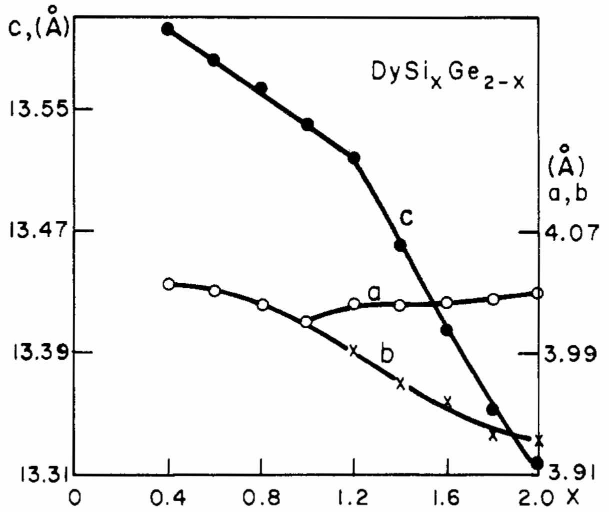

Figure 8.—Variation of lattice constants *vs.* composition of $DySi_xGe_{2-x}$.

The diagrams of the ternary phases of Sm–Dy can be very similarly interpreted. Here the tetragonal structure belongs to the digermanides and the germanium-rich region. The true composition of these digerman-

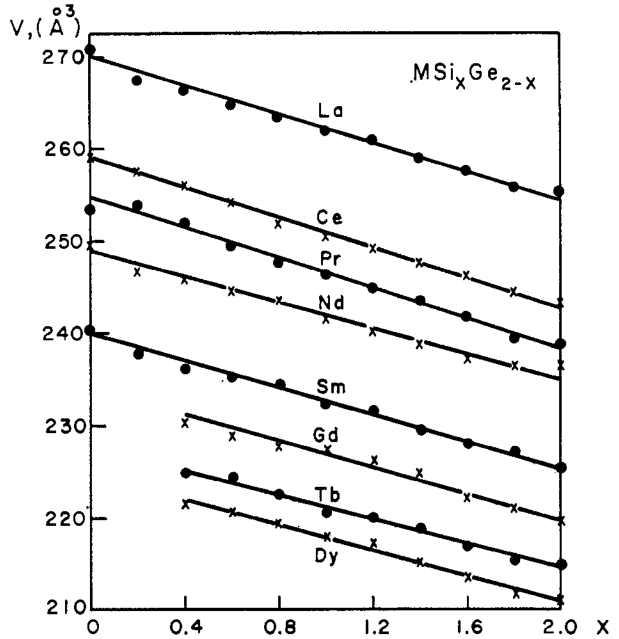

Figure 9.—Cell volume *vs.* composition for the MSi_xGe_{2-x} systems.

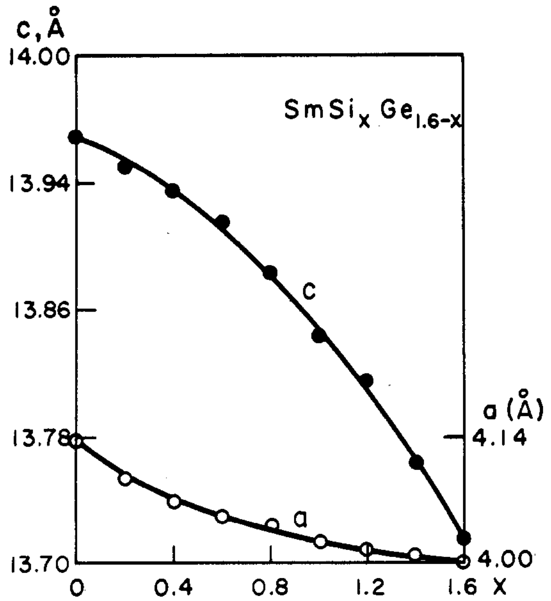

Figure 10.—Variation of lattice constants *vs.* composition of $SmSi_xGe_{1.6-x}$.

ides is not 1:2, and, because they are tetragonal, the Ge deficiency must occur equally in both nonmetal chains. Up to 50% Si and Ge, the substitution of Ge atoms by Si proceeds in the two chains. From 50 to 75%, Si enters only the chain depending on *b* and diminishing it. In this case, the size of the *a* axis regulates the decrease of the volume, despite the sharp decrease in *c* during the formation of Si–Si interchain bonds. Beyond 75% Si content, the Si atoms enter the *a*-dependent chain, but substitution by Si atoms is incomplete, and holes are formed, thus enabling the further regulation of the volume by the *a* axis. The assumed deficiency of Si atoms in this region is in good agreement with experimental results and with what is known for these compounds in the literature.[2,3]

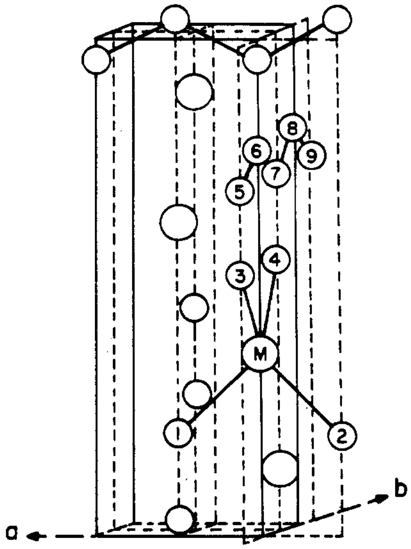

Figure 11.—The $ThSi_2$ structure.

Investigation of the Nd ternary phases reveals that the *c* axis is much larger than in the Sm–Dy phases, because of the larger Nd atom. Consequently the bonds between the nonmetal chains must be of the Ge–Si type; Si–Si bonds would require much smaller *c* values, as was observed. The Si atoms are first substituted in the *b*-dependent chains, and at equal germanium and silicon content they are completely filled with Si atoms. From here on, Si atoms enter the chains dependent on *a*, Si–Si interchain bonds are consequently formed, and *c* decreases sharply. The incomplete substitution of Si atoms in the *a*-dependent chains takes care of the gradual decrease in the cell volume.

The case of the ternary phases of praseodymium is very similar to what has been said for the Nd compounds. In this case, also, the orthorhombic splitting enables the formation of Si–Ge interchain bonds. The decrease of the *c* axis with growing silicon content is moderate (Pr having relatively large atomic radius) and stoichiometric silicides are therefore formed.

In the $SmSi_xGe_{1.6-x}$ series all of the compounds have the tetragonal structure. It must be assumed—in accordance with the tetragonal phase—that the nonmetals are distributed in the two chains equally and that the vacancies in these chains (the compounds are nonstoichiometric) are also equally distributed. The deficiency in Si atoms and in many of the M–Si interchain bonds causes only moderate decrease in *c* in the silicon-rich region.

The distribution of the silicon and germanium atoms in the nonmetal chains used in the interpretation of the ternary phases seems to be the main factor determining the crystal structure of the binary compounds too. In the disilicides of La–Pr, the M–Si bond and the *c* axis have an intermediate size ($R_{Si}/R_M < 0.725$), so that the *a* and *b* axes have no part in regulating the cell volume by their increase or decrease, and complete Si chains can form. Stoichiometric tetragonal structures form as a result.

The disilicides of Nd–Dy have relatively small *c* values ($0.750 > R_{Si}/R_M > 0.725$), so that the other two axes must increase, which is achieved by the formation of vacancies in one of the Si chains and by increase of the axis dependent on it. The structure of these silicides is therefore orthorhombic and nonstoichiometric.

In the digermanides of La–Ce, a large metal and a nonmetal are present ($0.750 > R_{Ge}/R_M > 0.725$). The value of *c* is large, and, in order to maintain the value for the cell volume, one of the other two axes must decrease. This is achieved, as can be seen from the orthorhombic structure, by the incomplete filling of one of the nonmetal chains by Ge atoms, so that these digermanides will be orthorhombic.

In the digermanides of Pr–Sm the length of *c* is of an intermediate value ($0.760 > R_{Ge}/R_M > 0.750$). The nonmetal chains—depending also on the *c* axis—are not large enough to accommodate all of the Ge atoms, and vacancies appear in both the *a*- and *b*-dependent chains, resulting in nonstoichiometric tetragonal structures.

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A Comparison of the Donor Properties of Dimethylcyanamide and Acetonitrile

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Thermodynamic and spectrochemical data on the donor properties of dimethylcyanamide, $(CH_3)_2NCN$, toward charge-transfer types of acids, conventional Lewis acids, and nickel(II) are reported. Evidence from changes in the infrared and nmr spectra upon coordination is interpreted to indicate that the nitrile nitrogen is the donor atom. The C^{13}–H coupling constants are very informative in elucidating the properties of this donor and the structure of these adducts. The donor properties of N,N-dimethylcyanamide are compared with those of acetonitrile and the differences are discussed.

Introduction

The nitriles as a group have been rather widely investigated as donors toward Lewis acids.[2,3] While classified generally as weak bases, they exhibit several unusual and interesting properties such as an increase in the nitrile stretching frequency ($\Delta\nu_{CN}$) upon coordination[4,5] and very large Dq values in metal complexes.[6] Since it is well known that the substitution of a methyl group in acetone by an N,N-dimethyl group to give N,N-dimethylacetamide (DMA) results in a marked increase in donor strength, it is of interest to examine the donor properties of N,N-dimethylcyanamide (DMCA) which is related to acetonitrile as DMA is to acetone.

Relatively little work has been carried out on N,N-dimethylcyanamide. Augdahl and Klaeboe[7] have reported thermodynamic parameters for the interaction of DMCA with I_2, ICl, and IBr which suggest that DMCA is a better donor toward these acids than is acetonitrile. However the authors were not able to establish the donor site in DMCA. Small increases in $\Delta\nu_{CN}$ were incorrectly taken to be indicative of σ donation from the nitrile lone-pair orbital. Bock[8,9] has prepared a novel series of compounds from nickel carbonyl and various cyanamides. In view of the above considerations, we decided to extend the study of the donor properties of DMCA to a wider range of acids and attempt to elucidate the donor site.

Experimental Section

A. Reagents and Solvents.—Dimethylcyanamide was obtained in a highly purified form (99.9% pure by vapor-phase chromatography) from American Cyanamid Co. A second sample of technical grade, obtained from Matheson Coleman and Bell, was purified by distillation at reduced pressure [bp 48° (10 mm)].

Hydrated nickel(II) perchlorate was obtained from G. F. Smith. Boron trifluoride from Matheson was purified by passing the gas through a drying tower containing concentrated sulfuric acid. Stannic chloride reagent grade from J. T. Baker was used as received. Phenol (Baker and Adamson) was distilled once at reduced pressure. The center fraction was retained and this was sublimed just prior to use. *p*-Chlorophenol from Eastman Organics was distilled at atmospheric pressure just before use.

N,N-Dimethylaniline (Fisher) and N,N-dimethylacetamide (Fisher) were distilled from barium oxide at reduced pressure before use. Trimethylamine, also from Fisher, was used as obtained. Trimethylamine N-oxide (Eastman Organics) was sublimed under vacuum before use. Nitromethane (Eastman Organics), chloroform and carbon tetrachloride (both from Mallinckrodt), methylene chloride (J. T. Baker), and acetonitrile (Fisher) were all stored over Linde V-A Sieves for at least 2 days before being used as solvents.

B. Typical Preparations of Lewis Acid Adducts. 1. $BF_3 \cdot$DMCA.—The boron trifluoride–dimethylcyanamide adduct was prepared in benzene dried over calcium hydride. Boron trifluoride, previously passed through a sulfuric acid tower, was bubbled slowly into the solution of DMCA in benzene at room temperature. The system was vented through a calcium chloride drying tube. A rapid flow of nitrogen was maintained through

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[1] Abstracted in part from the Ph.D. thesis of H. F. Henneike, Jr., University of Illinois, 1967.

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