High-Pressure Polymorphism in Sodium Chloride: A Reinvestigation

Abstract. *X-ray studies of sodium chloride near 20 kilobars were made in an attempt to verify the reported high-pressure-stable, cesium chloride-type structure. Experiments employing extreme shear forces, elevated temperature, and various moisture contents have shown no indication of a second phase. A reexamination of the original x-ray evidence suggests that the data may be explained by lithium found in the apparatus.*

The report of Evdokimova and Vereshchagin (*1*, *2*) of the observation of additional lines in powder patterns of NaCl taken above 17,700 kg/cm^2 (17.4 kb) has created a nagging uncertainty relative to the use of this material as an internal pressure calibrant for high-pressure x-ray diffraction experiments. If, as these authors suggest, these lines are caused by a partial transformation to a CsCl-type structure, a more satisfactory calibrant should be sought (*3*). Apparently substantiative evidence is found in the piston displacement work of Pistorius (*4*) and the shock experiments of Larson (*5*); however, the contradictory evidence which may be cited is extensive. Jamieson (*6*) noted that the transformation pressure of solid solutions of NaCl + KCl extrapolates, for zero potassium concentration, toward the 220- to 270-kb region where shock data (*7*) indicate a transformation occurs. Corll and Samara (*8*) observed no discontinuity in the curve of the dielectric and elastic constants of NaCl as a function of pressure to 26 kb. No confirming x-ray work exists in spite of the widespread use of NaCl as a calibrant (*9*). Finally, the observed data fit the proposed model poorly. This can be seen in Table 1, where calculated intensities are presented together with the observed data.

This conflicting evidence has led us to carry out a series of high-pressure x-ray experiments in an effort to reproduce the original work. The high-pressure x-ray camera employed the boron-annulus technique of Jamieson and Lawson (*10*) as modified by McWhan and Bond (*11*). The experiments are summarized below:

Sensitivity. With especially selected amorphous boron which has no detectable diffraction pattern of its own, it has been possible to observe less than 5 percent of a second phase based on observations of mixtures under pressure. Thus, there should be no difficulty in detecting the reported extra lines.

Shear. Rotation of the bottom anvil with respect to the top anvil while the NaCl sample is compressed to 20 kb between anvils results in extreme shear. No additional lines were observed for samples photographed at about 20 kb after being subjected to this treatment.

Temperature. Neither internal flash heating caused by resistive heating of a carbon diluent (*6*) nor external heating to a measured 170°C by means of resistance wires taped to the anvils produced any of the additional lines observed by Evdokimova and Vereshchagin. (The flash heating experiment, however, gave rise to additional lines which were all attributed to B_4C (*12*) formed as a result of the intense heat acting on the boron and carbon.) All photographs were taken at about 20 kb after the temperature had been quenched to 25°C.

Moisture. NaCl which was dried for a period of up to 2 weeks at 500°C exhibited no additional lines when photographed at about 20 kb and 25°C. The same results were obtained for NaCl to which water was intentionally added.

Since extremely favorable conditions have not permitted the reported additional lines to be observed, it seems reasonable to return to the original work for the explanation of their cause. The high-pressure chamber of Evdokimova and Vereshchagin consists of a 0.4- to 0.5-mm cylindrical hole in a beryllium rod (*13*). The sample is sealed off in this chamber by a steel stopper on top and, on the bottom, a lithium stopper that is in contact with a fluid reservoir containing a manganin pressure gauge. The location of the lithium plug is such that if any advance occurred while the pressure is applied and the loosely compacted NaCl is being compressed, the plug would be taken directly into the bottom of the x-ray beam. Further complications would be expected from the ubiquitous LiOH, which can only be removed from lithium by extreme measures. Diffraction from lithium (a = 3.51 Å) which is not centered in the beam could account for all the observed lines except three (d = 1.51, 1.107, and 1.021) which are very close to strong LiOH lines. The fit of the observed data by this explanation is at least as good as the earlier explanation based on a polymorphic transformation and, in addition, easily accounts for the "quenchability" which was reported. Our possible explanation could easily be checked by using a substitute for lithium in the original apparatus.

Table 1. Observed and calculated intensities for NaCl based on a CsCl-type structure. Abbreviations: N.O., not observed; Extr., extremely.

hkl	Observed *d* (*2*)	Observed intensity (*2*)	Calculated intensity
100	3.36*	N.O.	7
110	2.37	Medium	100
111	1.94*	N.O.	<1
200	1.66	Weak	14
210	1.51	Weak	<1
211	1.37	Weak	23
220	1.18	Weak	6
300, 221	1.107	Extr. weak	<1
310	1.06*	N.O.	6
311	1.021	Extr. weak	<1
222	0.981	Very weak	1

* d value calculated on the basis of a = 3.36 Å.

The piston displacement work of Pistorius (*4*) is also questioned, since both the present work as well as that of Jamieson (*6*) fail to detect a phase transformation, even though the experiments were carried out in the same temperature range.

The shock experiments of Larson (*5*) show a very small anomaly near 29 kb, for which the best explanation at present is a phase transformation. Because of the considerable difference in pressure (29 versus 17.4 kb), it is probably necessary to account for this result independently. Since this effect has only been observed under the special conditions of the dynamic experiment, it would not be expected to complicate static experiments.

In the absence of definitive supporting evidence, then, the x-ray data of Evdokimova and Vereshchagin do not establish the existence of a phase transformation in NaCl near 17 kb. In view of the conflicting exidence, it is more reasonable to account for the observed extra lines by the presence of an impurity such as the lithium plug of the apparatus.

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Genetic Code: Aspects of Organization

Abstract. *The pattern of organization of the genetic code decreases to a minimum the phenotypic effects of mutation and of base-pairing errors in protein synthesis. Single base changes, especially transitions, usually cause either no amino acid change or the change to a chemically similar amino acid. The degree of degeneracy of the codons for an amino acid is correlated with their guanine-cytosine content. The code gives greater protection (by both degeneracy and guanine-cytosine content of codons) to those amino acids that appear more frequently in proteins. Increased reliability of the protein-synthesis system afforded by this pattern of organization may have determined the fitness of the present code.*

Schroedinger (*1*) has pointed out that a fundamental characteristic of any mechanism of inheritance must be unusual stability in the face of natural randomizing influences. We now present evidence that the biochemical system for gene expression, the genetic code, is organized to stabilize the phenotype by lessening the effects of mutational processes. Although many elements of the code remain to be elucidated, it has been shown (*2*) that the distribution of codons is nonrandom (*2–5*). We now suggest that the pattern of the present code protects the organism against the consequences of mutation. In addition, the code minimizes the consequences of base-pairing errors occurring in the transcription and the translation of the information in DNA. Ambiguity in translation can be demonstrated in cells and extracts; it is further increased by mutations or drugs that alter the ribosome (*6*). Such noninherited errors were probably even more conspicuous during early stages of the evolution of mechanisms of protein synthesis (*7*). A code capable of buffering the effects of these errors would increase the reliability of the entire system for gene expression and thus be of selective advantage.

Table 1. RNA codon assignments. The RNA codon assignments are those designated principally by Nirenberg and by Khorana, and their co-workers (*2*). A question mark denotes incomplete evidence.

AAU Asn	ACU Thr	AGU Ser	AUU Ilu
AAC Asn	ACC Thr	AGC Ser	AUC Ilu
AAG Lys	ACG Thr	AGG (? Arg)	AUG Met
AAA Lys	ACA Thr	AGA Arg	AUA (? Met)
CAU His	CCU Pro	CGU Arg	CUU Leu
CAC His	CCC Pro	CGC Arg	CUC Leu
CAG Gln	CCG Pro	CGG Arg	CUG Leu
CAA Gln	CCA Pro	CGA Arg	CUA (? Leu)
GAU Asp	GCU Ala	CGU Gly	GUU Val
GAC Asp	GCC Ala	GGC Gly	GUC Val
GAG Glu	GCG Ala	GGG Gly	GUG Val
GAA Glu	GCA Ala	GGA Gly	GUA Val
UAU Tyr	UCU Ser	UGU Cys	UUU Phe
UAC Tyr	UCC Ser	UGC Cys	UUC Phe
UAG Trm	UCG Ser	UGG Try	UUG Leu
UAA Trm	UCA Ser	UGA (? Try)	UUA Leu

The pattern of codon assignment can protect against the phenotypic effects of mutations or reading errors in two ways: (i) degeneracy such that the new triplet still corresponds to the original amino acid, and (ii) codon arrangements such that the new triplet specifies an amino acid whose substitution in the protein does not affect its function. In addition, the base composition of triplets may directly influence the relative rates of errors, and thus the more stable codons may serve a protective function.

Sonneborn (*5*) has reviewed the selective advantages inherent in a highly degenerate code in which different codons for the same amino acid differ in only one nucleotide of the triplet. If each of the 20 amino acids had its own unique codon, and if the remaining 44 base combinations did not specify amino acids, most one-step mutations would lead to nonsense and therefore to unfinished polypeptide chains. In this way, a degenerate code featuring a minimum number of nonsense codons, probably only those essential for punctuation, would serve significantly to decrease the rate of appearance of a mutant phenotype. Furthermore, if the triplets corresponding to the same amino acid share at least two bases in common, then one-step mutations change the identity of the specified amino acids as seldom as possible. Every amino acid appears (Table 1) degenerate at least twice in just this fashion (*8*).

The twice-degenerate amino acids are all of the form *ab purine* or *ab pyrimidine*. This pattern of codon assignment provides the maximum possible protection against mutation in a twice-degenerate system. It affords some protection against transitions (substitution of a purine for a purine, or of a pyrimidine for a pyrimidine) but none against transversions (substitution of a purine for a pyrimidine or a pyrimidine for a purine). Similarly, amino acids having four codons would be most protected if their four degenerate triplets conform to the set *abx*, where *x* is any base (*9*). In such an arrangement, one-third of all transitions and transversions remain within the group. This pattern of degeneracy characterizes all the amino acids that have been shown to be four-times degenerate. Finally, two amino acids that appear to have sixfold degeneracy, Arg and Leu (*10*), have codons of the form *abx* and *a'b purine*. This arrangement is exactly that distribution of six codons which insures that a random base change in the set is least likely to produce a codon not of the set. Serine is also probably six-times degenerate, but of the form *abx, a'b pyrimidine* (*2*). Although highly protective, such an arrangement makes serine the one exception to the generalization that the form of degeneracy minimizes the frequency of base substitutions that lead to different amino acids.

The genetic significance of this pattern of degeneracy is summarized in Table 2, which presents the relative frequencies of new amino acids appearing as a result of single base changes. In these calculations we assume that all one-step mutations are equally likely and that all possible codons for a given amino acid appear in equal amounts. The diagonal represents the frequency with which a given amino acid mutates to itself. A comparison of the diagonals of *A* and *B* of Table 2 shows that the arrangement of the code gives greater insurance