different bond lengths, but they are essentially the same as in ordinary germanium (2.45 angstrom). The bond angles vary from 91 to 120 degrees. At the present stage of investigation the distances and angles have not been very precisely determined.

The new dense germanium proved to be quite stable at room temperature, but at moderately elevated temperatures it reverted to the cubic form. At a temperature of 125°C, about half reverted to the cubic form in 8 hours. At 200°C the dense germanium was transformed almost completely within 6 hours. More measurements of the rate of conversion as a function of temperature will be required to determine the activation energy of transformation from the tetragonal to the cubic form.

Measurements of the resistivity of the new dense material as a function of temperature showed that it behaves as a semiconductor. A typical set of data for low temperatures, obtained by S. J. Silverman, is shown in Fig. 3. Measurements at higher temperatures were meaningless because at these temperatures the material reverted to the cubic form. The dense germanium was tested for superconductivity at cryogenic temperatures by H. R. Hart, Jr. Tests made at temperatures down to 0.33°K gave no indication of transition to a superconducting state.

It is of interest to establish the relationship of this new dense form of germanium to the highly conducting form found at pressures in excess of 120 kbar. Judging from the resistance behavior—particularly the sharp and great increase in resistance during decompression—one would expect the final state to be different from the highly conducting high-pressure form. In the absence of direct experimental information on the density and crystal structure of the high-pressure phase, and without full experimental phase diagram data, the conclusion that the two forms differ is only tentative. Perhaps the set of transformations reported here in germanium is an example of the reaction mechanism proposed recently by Libby (*5*).

Meanwhile, we believe the pressure-temperature phase diagram may well be as constructed by Jayaraman *et al.* (*6*), who took into account the work of Hall (*7*) on the effect of pressure on the melting point of germanium, and the room-temperature transition of Minomura and Drickamer (*1*). This diagram calls for a triple point for Ge I (cubic)/Ge II (high-pressure form)/-liquid at 500°C and 115 kbar. The room-temperature transformation at 120 kbar would then be a transformation to a new solid state (Ge II), not a melting phenomenon. In this system, the new dense germanium would be a metastable, low-pressure form, which could be called Ge III (*8*).

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Azeotrope of Isopropyl Alcohol and Isopropyl Borate

Abstract. *An azeotrope which boils at 82.0°C (corrected) is formed from* i-*propyl alcohol and* i-*propyl borate. The azeotrope contains at least 5.4 percent by weight of ester.*

Several azeotropic systems are formed from alcohols with esters of inorganic acids, such as mixtures of methyl alcohol and methoxytrimethysilane (*1*) and of *i*-propyl alcohol and *i*-propyl titanate (*2*). Similar azeotropes of alcohols with borates have been reported. Two of these, that of methyl alcohol and methyl borate (*3, 4*) and that of ethyl alcohol and ethyl borate (*5*) are well characterized; others including that of ethyl alcohol and methyl borate (*6*), *t*-butyl alcohol and methyl borate (*7*) and *n*-butyl alcohol and ethyl borate (*6*) or *i*-amyl alcohol and ethyl borate (*8*) should be regarded with suspicion because of the probability of transesterification reactions (*9*) which occur in systems containing a free alcohol and the borate of a different alcohol. For example, *i*-butyl alcohol with ethyl borate is known (*10*) to form ethyl alcohol and *i*-butyl borate.

Azeotrope formation between *i*-propyl alcohol and *i*-propyl borate has not been reported; however, we have frequently observed boron in condensates distilling below 100°C from reactions of *i*-propyl borate in which there is release of *i*-propyl alcohol.

$$(i\text{-Pr O})_3\text{B} \longrightarrow$$

$$i\text{-Pr OH} \xrightarrow[< 100^\circ\text{C}]{(i\text{-Pr O})_3\text{B}} \text{volatile B compound}$$

We postulated formation of an azeotrope; several distillations were carried out to test the hypothesis.

Distillation of a 1:1 by volume mixture of *i*-propyl alcohol and *i*-propyl borate from a simple still yielded a condensate containing 0.76 milliequivalents of boron per milliliter (meq boron/ml). A similar 1:1 mixture of alcohol dried with CaH_2 and freshly fractionated ester was fractionally distilled through a short, helix-packed fractionating column. The condensation temperature remained at 82.0°C during the distillation, and the condensate contained 0.87 meq boron/ml. Finally, a mixture of 10 g of freshly fractionated *i*-propyl borate and 90 g of *i*-propyl alcohol dried with CaH_2 was fractionally distilled through a vacuum-jacketed column packed with wire gauze and containing 95 plates. The reflux ratio was about 30:1. The head temperature was steady at 82.0°C (corr.). Samples of the condensate were analyzed periodically. They averaged 1.63 meq boron/ml. The first and last fractions had the same boron content. Analysis of a weighed sample from one fraction indicated 0.31 percent boron, equivalent to a concentration of 5.4 percent *i*-propyl borate.

The increased concentration of boron in the distillate as efficiency of fractionation is improved suggests that its presence is not caused by entrainment. Any entrainment involves instead the presence of excess alcohol when low efficiency fractionation is carried out. This is not surprising considering the small difference in boiling points between alcohol and azeotrope. The observed boron content of the distillate may not be the maximum which can be obtained with a more efficient column. Similar entrainment behavior is usually observed in the azeotropic distillation of methyl alcohol and methyl borate used for boron analysis; the observed boiling point throughout the distillation is that of methyl alcohol owing to the large excess of alcohol and the use of a simple still.

Table 1. Ester content and boiling points of azeotropes in alcohol-borate systems.

Boiling point (°C)			Wt. ester in azeotrope (%)
Alcohol	Ester	Azeotrope	
	Methyl (4)		
64.7	68.7	54.6	75.7
	Ethyl (5)		
78.3	118.6	76.6	30
	i-*Propyl*		
82.4	140.8 (*12*)	82.0	5.4

If the three established azeotropes in alcohol-alkyl borate systems are compared, there is a marked decrease in ester content as the boiling points of the components increase (Table 1). It might be remarked in addition that boric acid is volatile in steam (*11*), behavior which is probably related to the ester-alcohol azeotropes.

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Specific Immunologic Unresponsiveness to Synthetic Polypeptide Antigens

Abstract. *The injection of two synthetic polypeptide antigens into adult rabbits treated with 6-mercaptopurine, or into newborn rabbits, resulted in immunological "unresponsiveness" to subsequent immunizations with these antigens. The "tolerant" animals were shown to be reactive toward the nonrelated antigen ovalbumin.*

The phenomenon of acquired specific immunological tolerance (unresponsiveness) toward nonliving antigens was reviewed recently by Smith (*1*). The various experimental models analyzed were mainly serum proteins of human and bovine origin. For the analysis of (i) the molecular requirements for the induction of tolerance, and (ii) the range of specificity of the tolerant state in molecular terms, more quantitative information concerning specific immunological unresponsiveness would be obtained if there were available well-defined chemical compounds capable of inducing immunological tolerance in experimental animals. Recent studies have shown that some synthetic polypeptides may be potent antigens of narrow specificity, and might be used to study further the chemical basis of antigenicity (*2, 3*). We report here the induction of specific immunological unresponsiveness to two synthetic polypeptide antigens.

The antigens used in this study, denoted p(Tyr,Glu)- -pLys and p(Tyr, Glu)-pAla- -pLys (*4*), are multichain copolymers of amino acids and were described previously (*3*). The multichain polymer p(Tyr,Glu)- -pLys is composed of side chains of peptides containing L-tyrosine and L-glutamic acid attached to the ε-amino groups of poly-L-lysine. Analysis of a sample (112) indicated an average molecular weight of 14,700 (*3*) and a residue molar ratio of Lys : Tyr : Glu of 1 : 1.1 : 2.3. In the second multichain copolymer, p(Tyr,Glu)-pAla- -pLys, side chains of poly-DL-alanine, attached to the ε-amino groups of poly-L-lysine, were elongated with peptides containing L-tyrosine and L-glutamic acid. Analysis of a sample (202) showed an average molecular weight of 33,000 and a residue molar ratio of Lys : Tyr : Glu : Ala of 1 : 1.7 : 2.4 : 19.

The induction of tolerance was attempted by exposing newborn rabbits to the antigens and by treating adult rabbits with 6-mercaptopurine and antigen (*5, 6*). The experiment of tolerance to p(Tyr,Glu)-pAla- -pLys in newborns was carried out with two litters. In one litter, four were test animals and four were controls. In the second litter there were two test and three control animals. The test animals were injected intraperitoneally with 40 mg of antigen within 24 hours after birth, and 45 days later they received another dose of 40 mg of antigen.

At 97, 120, and 140 days of age, the animals of the control and the test groups were challenged with an immunizing dose of 15 mg of antigen in Freund adjuvant (*3*). At various time intervals after each of these immunizations, the animals were bled and tested for immune response by precipitin reaction (*3*). The results (Table 1) were that none of the test animals showed any antibody, when tested after the third immunization at the age of 5 months. On the other hand, all the control littermates gave, after the third immunization, a typical precipitin reaction reflecting an immune response of at least 300 μg of antibody per ml of serum. The antibody response both in test and control animals was checked also by passive cutaneous anaphylaxis (*7*). All the controls gave positive reactions, while the test animals were negative. As little as 0.2 μg of antibody to p(Tyr,Glu)-p(Ala)- -pLys may be easily detected by this technique (*8*). It thus appears that the injection of p(Tyr,Glu)-pAla- -pLys at birth conferred immunological unresponsiveness towards this antigen.

Table 1. Unresponsiveness to p(Tyr,Glu)-pAla- -pLys, after exposure of newborn rabbits to antigen. On the 1st and 45th days, 40 mg of antigen was administered to the test animals and on the 97th, 120th, and 140th days, 15 mg was administered to the test and control animals. Antibody test and response are shown as indicated.

Litter 1		Litter 2	
Test	Control	Test	Control
	Antibody test on the 117th day		
4—	4—	2—	1+
			2—
	Antibody test on 129th day		
4—	3+		
	1—	2—	3+
	Antibody test on 148th day		
4—	4+	2—	3+

A second experiment was carried out in adult rabbits, aged 2 to 3 months. Ten experimental animals were each injected with 75 mg of antigen itnravenously and with 6 mg/kg of body weight of 6-mercaptopurine intramuscularly. The injections of 6-mercaptopurine were continued for 14 successive days. The animals were challenged with the first immunizing dose of 15 mg in adjuvant, 30 days after the initial injection of the antigen, and on the 52nd and 73rd day two subsequent challenges were made, each followed by antibody tests.

The results showed that seven out of ten animals were completely negative in precipitin tests, two were positive, and one doubtful. On the other hand, of nine control animals which were similarly immunized by three injections of antigen in adjuvant, eight were positive and one was negative.