*RAMAN SPECTRA AND STRUCTURE OF CERTAIN INORGANIC TYPES OF GLASS**

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INTRODUCTION

INORGANIC glass, particularly the silicate glass which is extensively used in science, technology, and household products, belongs, like organic polymers, to the extensive class of amorphous substances. Consequently much similarity should be found in the processes by which both types of substance are formed. Their structures, to some extent, should also be similar.

It is universally known that amorphous substances have no crystal structure. The very fact that some substances cool in an amorphous, glass-like form while others produce crystals can now be explained, in broad outlines, by the classical theory of Tamman.[1]

For a more detailed description of the properties of amorphous substances it is necessary to re-

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*This article is aimed at a more or less complete survey of work on Raman scattering in silicate glass. Investigations devoted to a study of glass by other physical and physico-chemical methods will be touched upon only as required by the principal purpose of this survey.

sort to their kinetic and relaxation characteristics. The physical principles of the corresponding concepts is known to have been formulated by P. P. Kobeko; they have found exhaustive experimental confirmation in the works of P. P. Kobeko and his students,[2] and a mathematical treatment in the works by M. V. Vol'kenshtein and O. B. Ptitsyn.[3]

The microscopic quantity that characterizes the process of vitrification is the viscosity of the melt. At certain temperatures called the vitrification temperatures and denoted by T_g the viscosity becomes exceedingly high ($\sim 10^{13}$ poises), and it becomes increasingly difficult for the molecules to change their orientation. The molecules "do not get a chance" to regroup and an equilibrium state that corresponds to a higher temperature "freezes".

From the molecular point of view, the sharp increase in the viscosity with decreasing temperature of the melt indicates merely an increase in the influence of the intermolecular forces. This increase is due to the reduced mean thermal energy of the molecules. When the ratio of thermal energy to the energy of molecular interaction reaches a

certain value, the melt cools in the form of glass.

It is quite obvious that the kinetics of the vitrification process should depend to an exceedingly high degree on the molecular structure of the substance. The more complicated the molecules, i.e., the longer the molecular chains and the more branches they have, the sharper the increase in the viscosity of the melt upon cooling and consequently, the easier the vitrification. Experience shows that this is indeed so. For example, an investigation of the homological series of fatty alcohols has shown that in general the higher terms of the series[2] have the greatest tendency towards vitrification. The inorganic types of glass are no exception. It is known for example that the easiest to cool in the form of glass are silicates with a large deficit of oxygen atoms, corresponding to a content of large and irregular groups of silicon and oxygen atoms in the melt. As the relative number of oxygen atoms increases, the tendency to vitrification decreases. In the limit, when the Si:O ratio becomes exactly 1:4 (orthosilicates), glass is formed only in rare cases. We shall consider this problem in detail later on.

Although the processes of formation of organic polymers and inorganic glass do not differ in principle, nevertheless they are not identical in detail. A very important specific feature of certain types of inorganic glass, particularly complex silicates, is that they are formed of metallic and non-metallic oxides, which give rise to a great variation in the character and strengths of the bonds. This leads to a great variety in the possible structure of the resultant amorphous body, a structure essentially determined both by purely geometric factors (the radii of the ions) and by their charges, by the degree of covalence (ionization), and by the binding energy.

Scientists who investigate the basic features of the structure of inorganic glass all have a unilateral approach to the problem—a tendency to emphasize some one of the aforementioned specific features of the given systems, rather than attempt to examine the problem as a whole, from a general physical review of the nature of the chemical bond and the structure of amorphous bodies.

The most frequent approach to the problem of structure of inorganic glass, from the point of view of crystal chemistry of ionic crystals, is based on the analogy between the structure of the crystal and the corresponding glass.

The simplest premise on which such an examination is based is that only electrostatic forces act between the ions. Actually, however, one must not lose sight of other forces, for example those due to the partially covalent character of the bond. Under certain cases the bond must be predominantly covalent. Then the purely-geometric factors no longer play a decisive role. We shall return to this problem later on.

Goldschmidt[4] already tried to relate the fact that certain oxides such as SiO_2 or B_2O_3 readily produce glass while others, say Al_2O_3 cannot be obtained in glass form under any circumstance to the ratio of the radii $R_A R_O$ in the oxide $A_n O_n$. It was found that this ratio ranges from 0.2 to 0.4 in all oxides capable of vitrification.

Cases are known, however, when this rule is not obeyed. Thus, the value of R_{Be}/R_O for BeO is 0.3, i.e., it lies in the required range, but nevertheless no glass-like BeO has yet been produced.

A similar criterion was applied by Sun and Silverman to multi-component glass.[5] Pincus attempted to characterize the tendency to glass formation by means of another quantity, the ionic potential, defined as a ratio of the ion charge to its radius.[6] Here two physical parameters are already taken into consideration, the ionic charge and its radius. Thus Pincus' attempt was a certain step forward.

Many substantial investigations of the glassy state, also based on crystal-chemical analogies, have been made by Dietzel.[7, 8] He has shown that certain properties of glass (viscosity, ability to flake or crystallize, etc.) can be described with the aid of a quantity called the "field intensity" of the cations (K^+, Na^+, Ca^{++}, Pb^{++}, Ba^{++}, etc.), specified at the distance at which the anion of the oxygen of the glass-forming oxide is located (and not at the distance R of the cation, as proposed by several earlier workers), and characterizing the Coulomb interaction between the cation and a single charge of the oxygen. All the elements of interest in glass melting were arranged by Dietzel in a series according to the value of the "field intensity." The position of the element in this series was compared with its tendency to become incorporated in the silicon-oxygen lattice of the glass.* It turns out that the stronger the field of the cation, the less pronounced is this tendency. Very "strong" cations are more prone to formation of their own lattice with the oxygen atoms. The corresponding types of glass flake readily. On the contrary, glass containing "weak" cations in coordination with the oxygens of the SiO_4 tetrahedra are homogeneous and do not flake.

It has already been noted above that many prop-

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*Dietzel does not distinguish between ionic or covalent bonds of elements and the structural lattice of the glass.

TABLE I. Differences in electronegative potential and in the
degree of ionization of the A–O bonds

Serial number	A–O bond	Difference in electro-negative potential, $X_A - X_O$	Degree of ion-ization in per-cent	Serial number	A–O bond	Difference in electro-negative potential, $X_A - X_O$	Degree of ion-ization in per-cent
1	N—O	0.5	6	12	Be—O	2.0	63
2	C—O	1.0	22	13	Mg—O	2.3	73
3	S—O	1.0	22	14	Ca—O	2.5	79
4	B—O	1.5	44	15	Sr—O	2.5	79
5	As—O	1.5	44	16	Ba—O	2.6	81
6	Si—O	1.7	50	17	Li—O	2.5	79
7	Ge—O	1.7	50	18	Na—O	2.6	81
8	Sb—O	1.7	50	19	K—O	2.7	83
9	Ti—O	1.9	58	20	Rb—O	2.7	83
10	Zr—O	1.9	58	21	Cs—O	2.8	85
11	Al—O	2.0	63				

erties of glass are qualitatively explained within
the framework of Dietzel's ideas. Yet, an explana-
tion of many factors involves difficulties. Thus, for
example, the properties of glass containing such
cations as Pb^{++}, Cd^{++}, Zn^{++}, and certain others
(with electron shells unlike those of the inert
gases), are incompatible with the positions of these
cations in the table of the cited papers. Dietzel
does not give any satisfactory explanation for these
deviations.

Summarizing this brief statement of Dietzel's
ideas, we must above all emphasize the undoubted
success that he attained in describing various
properties of glass. This success is evidence of
the substantial role of electrostatic forces in the
vitrification process. It would be erroneous, how-
ever, to expect complete agreement between these
ideas and experiment. In fact, the forces acting
between the individual structural elements of the
glass cannot be ascribed exclusively to electro-
static interactions. One must always take into
account the partially covalent character of the
bonds.

To understand more clearly the relation be-
tween these two factors we tabulate (Table 1), on
the basis of literature data on the value of the elec-
tronegative potential,[9] the values of the degree of
ionization of various A–O bonds. It is seen from
the data of the table that in most of the cases cited
the degree of ionization is less than 50% or slightly
above it. The bonds that have an ionic character
are for the most part essentially those formed with
participation of the alkali and alkali-earth ele-
ments. The first three elements of the table form
with oxygen a predominantly covalent bond. The
calculation of a "field intensity" for such bonds, as
was done in one of Dietzel's papers,[8] therefore
hardly has any physical meaning.

The fact that many properties, nevertheless, are
in satisfactory agreement with Dietzel's conclu-

sions can be explained apparently by the following
considerations. A comparison of the degree of
ionization of the bonds with the field intensity of the
cations, arranged in the same order, shows that
they vary in opposite directions, the variation in
field intensity being more prominent. For example,
for potassium these quantities are 83% and 0.13, for
boron they are 44% and (depending on the coordina-
tion number) 1.34 to 1.63 respectively.* We thus
see an approximately twofold reduction in the de-
gree of ionization of the bond, but an increase in
the field strength by one order of magnitude. In
other cases we observe qualitatively the same pat-
tern. Consequently, the relative role of the elec-
trostatic interaction in the formation of the A–O
bond exhibits a net increase, although a slower one
than that of the field intensity in Dietzel's table of
elements.

It is hardly worth while to compare directly the
vitrification ability with the degree of covalence of
the bonds, although some grounds for this are usu-
ally seen in the fact that the directional character
of most covalent bonds contributes to the formation
of a lattice or in any case, to large and irregular
groups. For many oxides this is apparently indeed
so (SiO_2, B_2O_3, GeO_2, etc.) There are, however,
exceptions to this rule. A striking example of this
kind is BeF_2. According to Pauling's data on
electronegative potentials, the Be–F bonds have a
ionization degree of approximately 80%.[9] Never-
theless it is relatively easy to obtain BeF_2 in the
form of glass.[10] Consequently, the covalent char-
acter of the bonds does not always play a substan-
tial role in the vitrification process. Any criteria
based on calculation of the covalence, although
usable, must therefore be approached with care.[11]

Deserving of attention is the fact that the litera-

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*The field intensity will be given here and throughout in
units of the elementary charge.

ture contains contradictory opinions concerning the character of the Be-F bonds. An estimate made on the usual assumptions, as noted above, shows that in this case the ionic character of the bond predominates considerably. This is a natural result, since the F atom is the most electronegative of all elements. Yet, according to Neumann and Richter,[12] a melt of BeF_2 is characterized by very small electronegative potential, which, so to speak, demonstrates the substantially non-ionic character of the Be-F bonds. In the paper cited above[10] Hagg calls attention to the acid properties of BeF_2, in contrast to the base properties of BeO. This circumstance would appear to confirm the results of Neumann and Richter.[12]

One might assume that an important role in vitrification processes is played not by the type of the bond between the metal and the oxygen, but rather by the strength of this bond. Actually, it was noted earlier that vitrification is caused by a sharp increase in the viscosity near the temperature T_g, a viscosity which in turn is directly dependent on the magnitude and irregular character of the molecular groups. In the final analysis it is to a certain extent immaterial what forces cause the formation of such groups. It is merely important that "seams" can appear between the individual molecules and that these "seams" are sufficiently strong.

To verify the extent to which these concepts are correct in the case of BeF_2, we calculated the Coulomb attraction between the Be^{++} and F^- ions and compared the data with those given by Dietzel for the A-O bonds. It turned out that the Coulomb attraction is in this case approximately 0.7 (in arbitrary units). For glass-forming oxides ($P_2O_5SiO_2$ and B_2O_3) the corresponding values, using the same units are according to Dietzel[8] between approximately 2 and 1.35, i.e., substantially larger.* It is thus impossible to explain the anomalous behavior of BeF_2 on the basis of the primitive ideas concerning the strength of the Be-F ionic bonds.

In a recently published, exceedingly interesting work by Winter-Klein[13] the ability of vitrification is compared with the structure of the external electron shells of the atoms. The author shows by means of numerous examples that a quantitative criterion of this kind can be the number of external p electrons per single atom. The greater this number, the stronger the vitrification ability.

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*Here, as in further calculations of this kind, small corrections for the effective coordination number are generally disregarded.

If this number is less than or equal to two, no vitrification takes place at all.

It is most natural to attempt to express the rules established in the work by Winter-Klein in terms of the role of the strength and directional character of the covalent bonds.

In fact, it is well known from quantum-mechanical theory, that covalent bonds between two atoms are stronger, the more their orbits overlap. The p orbits overlap the s orbits more strongly than the s orbits overlap among themselves. The p-p orbit overlap is even stronger. If the strength of the s-s bond is taken to be unity, then the strength of the s-p bond becomes 1.73, and that of the p-p bond 3. The bonds become even stronger because of the interpenetration of the orbits. Differing greatly from the s orbits in their angular distribution, the p orbits determine furthermore the orientation of the bonds.[9]

Thus, generalizing the observations of Winter-Klein, it would appear that one can state that the number of p electrons per single atom of a given molecule characterizes the "average" strength and directional character of the bond. It is, indeed, these parameters of the bonds that can become important in vitrification processes.

If this is so, then one cannot lose sight of the fact that other outer orbits, such as the d and f orbits, can play an analogous role in the strengthening of the bonds and in making the bonds directional. By way of examples in which the d and f orbits must be considered, we indicate such important elements in glass production as titanium and vanadium, and also zirconium and molybdenum, for which the outer orbits are 3d and 4f respectively.

Under certain conditions these orbits, owing to interpenetration, may be even more effective than the p orbits.

Let us attempt to apply the above considerations to certain simple systems.

From the data of Table II it is seen that the application of the Winter-Klein criterion to certain simple systems is not in satisfactory agreement with experiment. Thus, for example, the boric anhydride is characterized by a criterion value of 2.8 while quartz has a value 3.3. Yet the former apparently produces glass more readily, as evidenced by the fact that it does not crystallize under almost any conditions; V_2O_5, which has the highest value of this criterion, produces no glass at all.

Thus, a criterion based on taking into account only the structure of the external electron shells of the interacting atoms cannot be considered universal.

TABLE II. Estimate of certain simple systems with
the aid of the Winter-Klein vitrification
criterion[13]

Serial number	System	Number of atoms	Number of p and d electrons	Number of p and d electrons per atom	Remarks
1	B_2O_3	5	14	2.8	Vitrifies readily Practically does not crystallize
2	SiO_2	3	10	3.3	Vitrifies readily Crystallizes
3	TiO_2	3	10	3.3	Does not vitrify
4	Bi_2O_3	5	18	3.6	Does not vitrify
5	V_2O_5	7	26	3.7	Does not vitrify

A special position is occupied in the rather extensive literature on the structure of glass by the principles postulated by Zachariasen.[14] The starting point in these principles is the assumption that the energy of the glass lattice is commensurate with the energy of the corresponding crystal. More accurately expressed, it exceeds it slightly, which explains, generally speaking, the merely weak tendency of glass to pass through crystallization. According to Zachariasen, a non-periodic lattice satisfies this condition.

For a long time, the view of Zachariasen that glass is a non-periodic lattice was contrasted with the crystallite concepts which, as is well known, were first formulated by A. A. Lebedev[15] and later on intensely developed by his students and followers.[16]

According to the initial version of the crystallite theory glass was considered, from the structural point of view, as a mass of very small crystalline formations of various silicates, whose nature is directly related to the composition of the glass. Subsequently the opinions of most investigators leaned towards the idea that the concept of crystallites should not be reduced to that of microcrystals with phase boundaries, but the crystallite is more correctly taken to be a regularized nearest-order region inside a general irregular and non-periodic lattice.[16] The quantitative relation between the regular and irregular structure of glass is still unclear.

Thus, the contrasting of these points of view has lost its meaning. Either one can be considered correct, each showing different aspects of the general problem.

In connection with this we note that the ability of crystallite formation is not an exclusive property of silicate or inorganic glass. Organic polymers also display such a property. There, too, the crystallites are assumed to be nearest-order re-

gions. Nevertheless, the presence of such regions did not in any way affect the conventional theoretical treatment of the structure of organic polymers.[2]

Summarizing briefly the papers surveyed above, which by far do not exhaust the literature on this probelm, we can state that not one of the criteria considered, which in the opinion of their authors characterize the ability of various elements to produce simple and complex types of glass, is in satisfactory agreement with experiment. This is why direct methods of investigating the structure of various glass-like bodies, which would permit the establishing of an atomic-molecular "architecture" of glass and which would also permit estimating the character of the bond between its individual structural elements, become particularly important. Spectroscopic methods can play a substantial role in this respect.

1. FEATURES OF THE RAMAN LIGHT-SCATTERING METHOD AS APPLIED TO THE INVESTIGATION OF GLASS

All the necessary information on vibrational spectra are contained in two monographs, references 17 and 18. We shall not discuss this problem.

There is also a rather extensive literature[19] devoted to experimental means and methods used to obtain and investigate Raman spectra. Not taking it upon ourselves to explain all aspects of this great and specialized problem, we confine ourselves merely to a few remarks connected with the specific nature of scattering in glass.

The considerable difficulties in obtaining scattering spectra in glass are due to the low intensity of the bands. One of the methods of reinforcing the bands consists of intensifying the illumination of the specimen. However, the use of several

high-power high-pressure mercury lamps for this purpose, the usual procedure in the investigation of liquids, hardly settles this problem, for the spectrum of these lamps contains a rather intense continuous background in addition to sharp lines. This background always interferes with the observation of weak scattering bands. It is particularly harmful in the study of glass, since the specimens as a rule have defects (knots, bubbles, etc.) which reinforce the parasitic scattering.

Most effective in the investigation of glass are high-power, low-pressure mercury lamps. They were first used for this purpose in the United States[20] and then by the authors of reference 21. These lamps are not only practically free of a continuous background, but at the same time produce a very strong radiation flux. A description of low-pressure mercury lamps can be found in the original papers.[22]

Light can be resolved and recorded photographically either with prism spectrographs or with diffraction-grating spectrographs. When glass is investigated, it is essential that the spectral instruments have a sufficiently high aperture. Otherwise the exposure time needed to photograph the spectra may reach many hours, and it becomes difficult not only to measure but even to estimate the intensities and polarizations of the bands.

The experimental conditions are considerably facilitated if photography is replaced by the photoelectric method of spectrum recording. In this case, firstly, the time required to obtain the results is considerably shortened and, secondly, exact quantitative measurements become possible.[21, 23, 24]

Unlike the photographic method, the photoelectric method is based on the use of a different spectral instrument, the monochromator. In principle the monochromator is essentially a spectrograph in which the photographic camera is replaced by an exit slit and its dispersing element (prism or diffraction grating) rotates. Thanks to this, the exit slit separates, in sequence, the radiation of a given spectral composition. After separation, the radiation is made to fall on a photoelectronic multiplier. The electric signal is amplified with a vacuum tube amplifier and is usually fed to a vacuum-tube recording potentiometer, which displays the spectrum on a paper chart.

The considerable noise found in the investigation of low-grade glass specimens is due to the fact that the defects in the specimens intensify greatly the mercury lines in the scattered light. These lines, upon entering the spectral instrument, produce an additional parasitic background. To eliminate this noise the authors of references

25 to 27 used the principle of double monochromatization of light. Double monochromatization of light, combined with the use of a low pressure lamp, has reduced the continuous background in such a radical manner, that it becomes possible to investigate, even in very low-grade specimens, the low frequency region of the spectrum directly adjacent to the exciting line.

Let us now touch briefly on the problem of frequency measurement and the degree of deplorization of the bands in the spectra. In the photographic method of measurement the frequencies are obtained by comparing the photographs of the spectra. In this case, generally speaking, great accuracy can be obtained. However, the bands in the Raman spectra of glass are broad and diffused. When measuring the frequencies of such bands difficulties usually arise, owing to a certain degree of arbitrariness in the aiming of the cross-hair of the comparator on the intensity maximum of the band. This is why frequency data obtained photographically are, as a rule, inaccurate. Yet the photoelectric technique of recording the spectra, being free of this shortcoming, is connected with a different source of possible errors in the measurement of frequencies, namely the non-linearity in the operation of the chart-advancing mechanism of the recording potentiometer. To exclude this source of errors, the authors of reference 25 to 27 have decided on a compromise: they measured the frequency visually, following the motion of the recording-potentiometer pen and fixing its position at the maximum of the band by means of a revolution counter, which was part of the double monochromator employed.[28] The greatest measurement error did not exceed 4 cm^{-1}, which is quite acceptable when studying scattering spectra in glass.

As mentioned above, the photographic polarization measurements encounter great experimental difficulties. These difficulties are due to the errors in the photometry of the emulsions. Since the spectra of the glass are of low intensity, the photometry is carried out under very unfavorable conditions (large-grain emulsions) and the sought quantities (the degree of depolarization of the bands) vary only over a narrow range (from 0 to 6 or 7), the accuracy of such measurements cannot be satisfactory. No wonder, then, that the literature contains only two known papers in which an estimate is made by photographic means (and a qualitative one to boot) of the state of polarization of bands in scattering spectra of certain glass-like bodies.

Measurement of the degrees of depolarization becomes further complicated by the specific re-

quirement that the radiation illuminating the object must have a definite direction. This requirement can be satisfied only if the aperture of the apparatus is reduced below normal. If illuminating devices with large apertures are used in the "classical" procedure of measuring the degree of depolarization, in which both components are obtained simultaneously (for example, with the aid of a Wollaston prism in the beam of scattered light), the increase in the aperture ratio is achieved at the expense of reducing the already narrow range of possible values of the degree of depolarization of the apparatus.

It is much better to carry out polarization measurements using a procedure based on the use of polaroid films of different orientations in the illuminating beam, so that the specimen can be illuminated with wide beams. This procedure is particularly convenient if photoelectric recording of the spectra is used.[29] This procedure also permits accurate intensity measurements. Without going into details, we merely note that the exact values of the degree of depolarization of the beams is determined in this procedure with the aid of a . calibration curve, which can be readily plotted beforehand. In those cases where exact quantitative data are not required (for example when solving most structural problems), it is possible to dispense with the calibration curve. This is exactly what the authors of references 21 and 24 to 27 have done.

Polarization methods in such objects as glass involve still further difficulties owing to the presence of strains of various intensities in the specimen, which are capable of distorting the polarization state of the bands (particularly of the strongly-polarized ones). Strains are expected to exert the maximum influence in readily-crystallized specimens, the production of which in the glassy state is possible only through abrupt cooling. This is why all quantitative comparisons of different specimens are doubtful or in any case should be carried out with care. The authors of references 21 and 24 to 27 restricted themselves only to qualitative estimates.

2. RESULTS OF EXPERIMENTAL STUDY OF RAMAN SCATTERING IN GLASS

A. General Character of Scattering, Multi-Component Silicate Glass and Fused Quartz

Most of the earlier investigators of Raman scattering in glass concerned themselves with complicated, multi-component systems. Nevertheless, they succeeded in establishing the specific features of this phenomenon. Therefore, adhering where possible to the chronological order, we begin the survey with these investigations.

The first attempts to investigate Raman spectra in silicate glass date back to 1928.[30-33] However, the results then obtained were contradictory and gave no definite indication even whether Raman scattering spectra exist at all in glass, let alone the character of this scattering. Thus, for example, Raman[31] and Raman and Krishman[32] suggest that Raman spectra in glass are characterized by diffuse bands, while Pringsheim and Rosen,[33] in spite of very prolonged exposures, could not detect even traces of bands in the investigation of fused quartz. One can consider the first reliable and clear data to be those obtained in 1929 by E. F. Gross and M. F. Romanova,[34] who investigated specimens of borosilicate crown glass, light and heavy flint glass, and fused and crystalline quartz. They actually observed broad smeared bands in the spectra of these substances, approximately in the same positions as the lines of crystalline quartz, but varying greatly in intensity from substance to substance. The spectrum of crown glass turned out to be much weaker than that of flint glass, and this was confirmed by subsequent investigations.

The character of the spectra (smearing of the bands), together with x-ray structural-analysis data, proves without doubt, in the Gross' and Romanova's opinion,[34] the amorphous structure of the investigated glass. The fact that the frequencies in the spectra of the glass coincide with those in crystalline quartz proves that the region amenable to investigation does not contain the frequencies that are characteristic of the vibrations of the quartz crystal lattice, but contains only the frequencies belonging to the internal vibrations of the individual SiO_2 groups.

In connection with this we note the following. The concept of crystal-lattice vibrations is applicable, strictly speaking, to molecular crystals, for which the internal vibrations can be separated from the external ones. A quartz crystal is essentially a gigantic molecule made up of atoms joined by bonds of equal type; this molecule is characterized by a regular alternation of the SiO_4 tetrahedra. The concept of vibrations of such a crystalline lattice therefore ceases to be precise.

The most complete and systematic research on glass of various complicated compositions was carried out by Bhagavantam,[35] Kujumzelis,[36, 37] Langenberg,[38] and Norris.[39] Let us dwell on some of these investigations.

Kujumzelis[36, 37] investigated 19 specimens of multi-component glass, including a system that

contains predominantly PbO and SiO_2 in various ratios, potassium-phosphate glass with a small addition of other cations, glass-like B_2O_3 and SiO_2, and certain other types of glass. In spite of the complexity of composition of most specimens, he succeeded, nevertheless, in establishing many general features of scattering in glass and in propounding certain ideas concerning the structure of glass, some of which make up an acceptable working hypothesis.

Kujumzelis observed for each of the investigated specimens a characteristic spectrum that consists, in agreement with the observations of E. F. Gross and M. F. Romanova,[34] of broad bands of different intensities. Perhaps the most interesting and newest detail that he has found is a continuous Raman spectrum in lead glass, in the form of a broad continuous band with maxima directly adjacent to the exciting line; this band has a sharp boundary at approximately 550 cm^{-1}.

Since the spectra of the glass do not exhibit a clear similarity with the spectrum of fused quartz and depend, furthermore, on the composition of the glass, Kujumzelis proposes that glass contains, in addition to coupled SiO_4 tetrahedra, other groups, groups consisting primarily of atoms (anions) of oxygen, which can be contained inside the cations of the metals and of the glass-forming oxides. Here the author leans on several remarks by Bragg, made in his well-known monograph on the structure of silicates.[40] Two of the bands, with frequencies of 610 and 800 cm^{-1}, which retain their positions almost exactly in the spectra of all types of glass including fused quartz, are ascribed by the author to those vibrations in which only oxygen atoms participate, for example six-term rings made of oxygen atoms.

Kujumzelis approaches the explanation of the aforementioned continuous scattering from the point of view of Zachariasen, and assumes that this scattering is due just to the superposition of the vibrations of the irregular and anomalous lattice of SiO_4 tetrahedra, a lattice which is a characteristic of glass. The sharp boundary of the continuous scattering band should obviously be compared with the vibrations of the individual SiO_4 tetrahedra as a whole.

While the interpretation of the continuous scattering and the assumed existence of different groupings in the glass is sufficiently plausible and can be considered acceptable, the attempt to detail the concept of such groupings appears to us unfounded and speculative.

Langenberg[38] investigated even more glass samples, also with complex but controlled com-

position. He found certain insubstantial corrections to the data obtained by Kujumzelis.[36,37] In the interpretation of his own results, Langenberg starts with the assumption the spectra of the glass contain frequencies of isolated tetrahedra, the values of which can be found in the paper by Schafer, Matossi and Wirtz.[41] The particular fact that the bands in glass acquire a diffused character (compared with crystalline quartz) is indeed evidence, according to Langenberg, of variations in the symmetry of the tetrahedra and the splitting of the degenerate vibrations of the glass.

One can hardly agree with an interpretation of the spectrum of the silicates and silicate glass based on the frequencies of an isolated SiO_4 tetrahedron. It is impossible, even in rough approximation, to separate the free tetrahedra in any glass (with the possible exception of orthosilicate glass) and more so in quartz, since all tetrahedra are partially or completely bound to each other by the common oxygen atoms. It will be shown later on that in practically all orthosilicates the internal vibrations of the individual tetrahedra do not appear. It is therefore more correct to consider the vibrations of the entire set of tetrahedra simultaneously. Since, however, many authors still use the concepts of isolated SiO_4 tetrahedra, referring, for example, to experimental data on the vibrational spectra of silicane ethers, we shall again return to a more detailed analysis of this problem.

The experimental results of Kujumzelis and Langenberg were essentially confirmed by Norris,[39] whose work we shall not discuss here.

There are many very interesting and extensively publicized investigations on the effect that annealing of glass has on its structure. There are only two papers by Prod'homme specially devoted to the study of glass of complex composition by the Raman scattering method. A description of the results of analogous experiments with fused quartz is found in one of the papers of Kujumzelis.[37]

According to Prod'homme, the hardening of the specimen leads to a unique effect in the Raman spectra, namely, to a certain broadening of all bands. No frequency shifts or redistribution of intensities among the bands is observed. Yet Kujumzelis[37] did not observe any changes in the spectrum of fused quartz at all. Prod'homme tends to attribute his results to a reduction in the degree of ordering of the SiO_4 tetrahedra in the hardened specimens.

Since the literature on the application of the Raman scattering method to the study of this problem is skimpy and since the results obtained

are to some extent contradictory, we confine ourselves to these remarks.

B. Two-Component Silicate Glass

The undisputed shortcoming of the papers discussed above is the not too felicitous choice of glass types, of too complex compositions. It is true that this circumstance did not prevent establishing the general character of scattering in glass-like substances, but it has undoubtedly made it difficult to determine their structure. A favorable exception if the investigation of two-component sodium and lead-silicate glass by M. F. Vuks and V. A. Ioffe.[44] Sodium glass was represented by seven specimens, Na: 23, 27, 33.3, 37.6, 42.9, 45.5, and 50. The lead-silicate group, in view of technological difficulties, comprised only three specimens, Pb: 35, 40, and 50.*

This research has established that the spectra of sodium-silicate glass contain four bands each, while those of lead-silicate glass have two bands. As the silicon content increases, the frequencies and intensities of the bands change systematically. In the limit, at the maximum silicon content in the glass, the frequencies of several of the bands approach the values characteristic of amorphous and crystalline quartz. One of the bands with a frequency of approximately 1090 cm^{-1}, is particularly intense in the spectra of the sodium-silicate specimens that are rich in sodium oxide. Apparently no analogue can be found for it in the quartz spectrum. The bands of lead-silicate glass are shifted towards the lower frequencies, relative to those of solium-silicate glass. M. F. Vuks and V. A. Ioffe correlate this to the replacement of the relatively light sodium atoms by the considerably heavier lead atoms.

To judge more reliably the possible structural changes in sodium-silicate glass, Vuks and Ioffe plotted the frequency variations of the four observed spectrum bands as functions of the composition of the glass (Fig. 1). Before discussing this plot, we make the following comment. In the investigation of various properties of multi-component systems it is assumed that these properties vary with the composition continuously and monotonically, so long as no new components appear or no old components vanish in the system. It is natural to think that deviations from the monotonic variation in the character of the Raman spectra (frequency, intensity, and polarization of the bands) can also serve, for some compositions, as a

*Here and throughout the numbers denote the molecular percentages of the metal oxide.

FIG. 1. Plot of the frequencies of certain bands in the spectra of sodium-silicate glass vs. composition.[44]
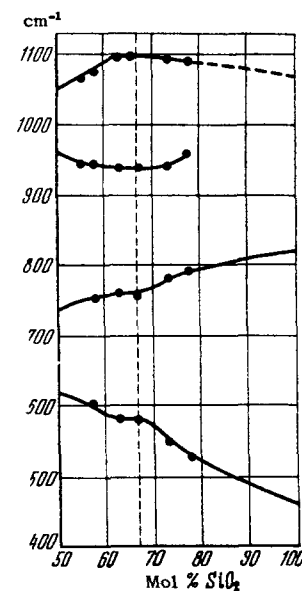
criterion of certain structural transformations in the system. Naturally, further data are necessary to establish accurately what transformations do, indeed, take place.

It is seen from Fig. 1 that as composition of the glass approaches that of the sodium-bisilicate type $(Na_2O \cdot 2SiO_2)$, the frequency variation for all bands without exception, is no longer monotonic with the composition. This, apparently, is evidence of a structural transformation in the bisilicate region. Vuks and Ioffe believe that the bisilicate composition corresponds to the formation of a chemical compound in the glass. Incidentally, later one of these authors later refuted such an interpretation of the results.[45]

The idea of investigating sufficiently simple systems was further developed by E. F. Gross and V. A. Kolesova.[46, 47] They investigated sodium and potassium-silicate glass and also one sample of lithium glass and fused quartz. Their research has established that the frequency and intensity of the spectrum bands vary with the alkali content in the glass. For the sake of clarity, all their data are shown schematically in Fig. 2, while the frequency dependencies are shown in Fig. 3. Both figures are taken from references 46 and 47. It is evident from these data that the variations in the spectra are essentially monotonic. Only in compositions approaching the metasilicate do certain frequencies vary sharply. The specific frequency variation observed by Vuks and Ioffe[44] in the region of the sodium bisilicate is thus unconfirmed.

Comparison shows great similarity between the spectra of sodium-silicate and potassium-silicate glass, and also with the spectra of one
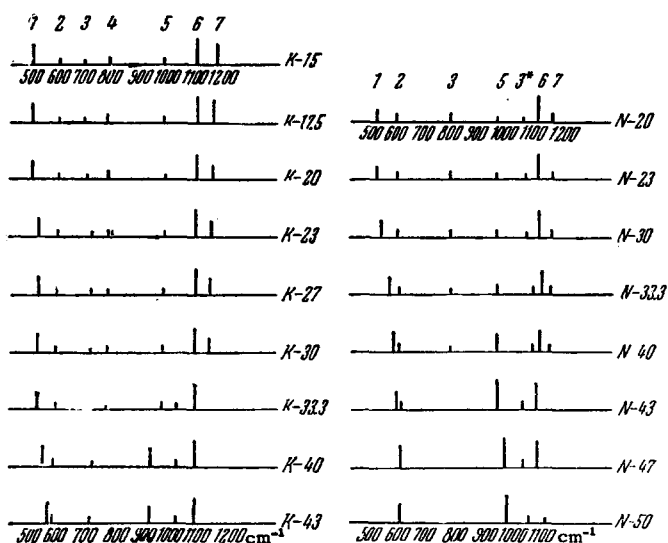
FIG. 2. Schematic representation of the spectra of sodium and potassium silicate glass.[46]

type of lithium glass. Yet lithium, sodium, and potassium differ quite substantially in their atomic weights. This means that the cations of the alkali metals form strong ionic bonds with the oxygen, and consequently their vibrations are inactive in Raman scattering. In other words, Raman spectra of alkali-silicate glass contain only the vibrations of the silicon-oxygen skeleton. This is exactly the interpretation proposed for this fact by Gross and Kolesova.[46, 47]

Incidentally, in the later one of these two papers,[47] Gross and Kolesova indicate that the spectra of the two specimens of Na-20 and K-20 glass display weak smeared bands near ~ 300 cm^{-1}. This can be ascribed to vibrations of the Na—O and K—O bonds, respectively. Since, however, a strong background of parasitic scattering appears when this region of the spectrum is investigated by the ordinary photographic procedure,[47] these results may be in doubt.

Even if the vibrations of the Me$_{alk}$—O bonds are actually inactive, this gives no grounds whatsoever for generalizing the results to include any other cation. Furthermore, investigation of glass containing different cations, which will be discussed later, proves without doubt the ability of many cations to become incorporated into the silicon-oxygen grid through partially covalent bonds.

Thus, the work of Gross and Kolesova leads to the important conclusion that the Raman scattering, at least in the case of alkaline-silicate glass, displays essentially the vibrations of the silicon-oxygen skeleton. This conclusion, reinforced by further research made by other authors,[21, 24, 25] has served as the base for a theoretical calculation of

the spectral frequencies of certain silicates and glasses of known composition.

The most general point of view, which is consistently developed by Gross and Kolesova, is that to each band in the spectra of the investigated glass there is a corresponding band (analogue) in the spectrum of fused quartz. Since, as already noted, the spectra of glass display gradual variations with the composition, this might appear to prove the existence of a continuous structural transition from fused quartz to glass. Thus in the opinion of the Gross and Kolesova[46, 47] glass is, from the structural point of view, a spatially deformed silicate lattice with partially broken Si–O bonds (owing to the oxygen atoms in the oxide of the metal), in which cations are statistically distributed. In the limit, when the glass approaches the metasilicate in composition, such a lattice is gradually transformed into an infinite chain. This is just the point of view of Zachariasen,[14] which was later developed by his successors[48] and applied to complicated glass. This concept is particularly clearly formulated by Gross and Kolesova.[47]

In all the above investigations the spectra were recorded photographically. The authors could therefore study only the frequency variation, and instead of accurately measuring the intensities they confined themselves to semi-quantitative estimates. The situation was particularly unfavorable in connection with polarization measurements. Until recently the literature contained only two references to investigations in this direction. One[20] deals with research on polarization spectra of two random specimens of complex glass, and its results are therefore of value from the procedural point of view rather than from the scientific one. The second work[49] is devoted to an investigation of fused quartz, and will be referred to repeatedly.
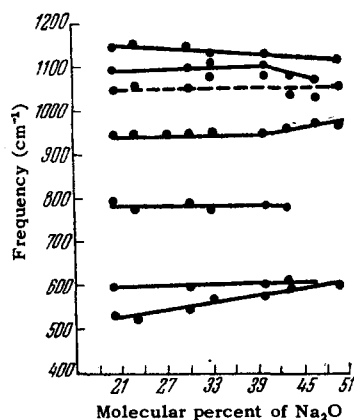

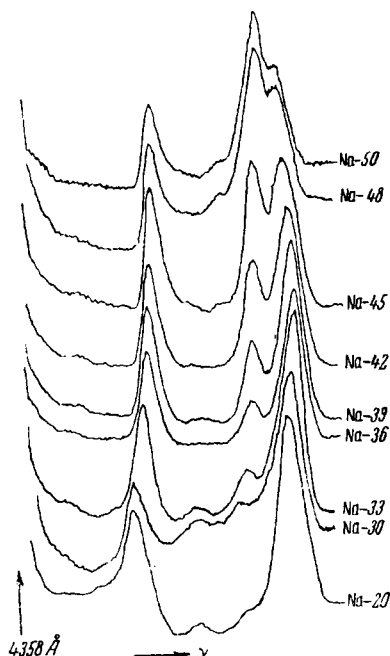FIG. 3. Dependence of certain bands in the spectra of sodium-silicate glass on their composition.[46,47]

FIG. 4. Photoelectric records of spectra of several sodium-silicate types of glass.[25]

Only with the development of the photoelectric method of recording spectra did it become possible to fill the gap in the field of polarization measurements. At first these new experimental procedures* were applied to investigations of sodium-silicate and potassium-silicate glass.[21, 24, 25]

The first of these systems, which was studied in particular detail, was represented by 22 specimens, starting with glass (Na-12) and ending with metasilicate (Na-50). The composition was varied in steps of one to three molecular percent. In addition to these systems, spectra of lead metasilicate (Pb-50) and fused quartz were investigated.

The spectra of several sodium-silicate and of two potassium-silicate types of glass, (obtained in natural light), taken for references 21, 24, and 25, are shown in Figs. 4 and 5. The details characteristic of the scattering are clearly seen. In spectra of alkali-poor specimens, and also in complex lead glass or fused quartz,[36-38] a continuous Raman spectrum is seen adjacent to the excited line. This apparently does not appear at once, if the series of spectra is examined from the metasilicate side, but only starts with glass containing approximately 30% of alkali. Then, as the glass becomes poorer in alkali, the spectrum becomes more intense, but nevertheless of lower intensity than the analogous scattering in fused quartz. This is illustrated in Fig. 6, which shows

*All polarization measurements reported here and throughout were carried out with an illuminating beam of large aperture.
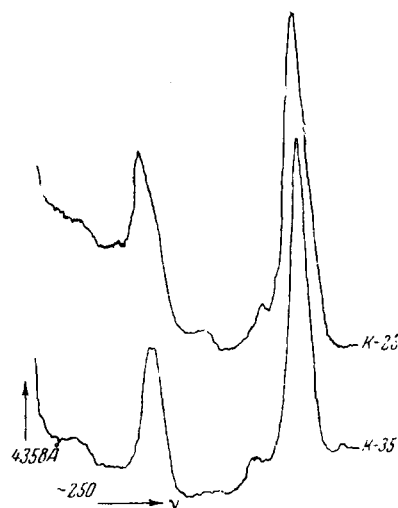

FIG. 5. Photoelectric records of spectra of two potassium-silicate glass specimens.[25]

the spectra of specimens of fused quartz and K-15 glass of equal size, obtained under identical conditions. Thus, an impression is gained that the continuous Raman spectrum is a specific feature of the spatial coupling of the SiO_4 tetrahedra.

It is also seen in Figs. 4 and 5 that a small diffused maximum is observed at low frequencies (approximately 250 to 300 cm^{-1}), particularly in spectra of potassium glass. Since the intensity of this maximum does not change noticeably with varying cation concentration,[25] it is apparently wrong to attribute it to vibrations of the Me—O bond, as has been done by Gross and Kolesova. It will be shown below that the polarization measurements confirm the correctness of these conclusions.

We now call attention to another important feature of the scattering spectra of specimens with low alkali contents, as compared with spectra of fused quartz, namely the very high intensity of the 1096 and 1170 cm^{-1} bands. It exceeds in intensity the "analogue band" of fused quartz by a factor of approximately 25. In our opinion[25] this shows that this group of bands in the spectra of fused quartz and glass is connected with different forms
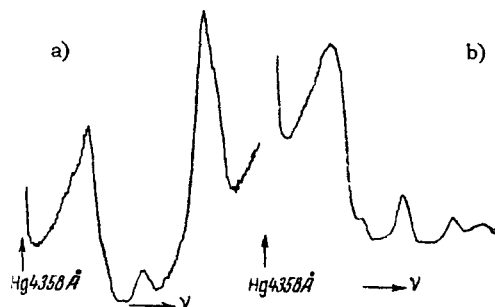

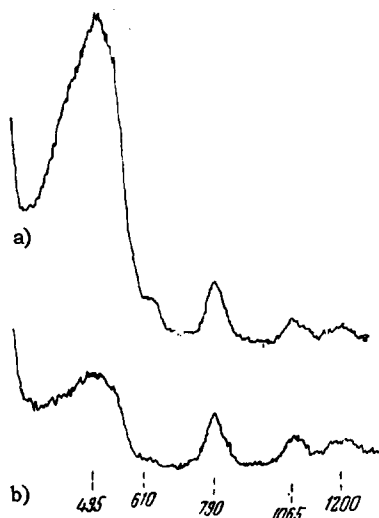FIG. 6. Comparison of spectra a) of fused K-15 glass and b) quartz, obtained under identical conditions.

FIG. 7. Photoelectric recording of polarization spectrum of fused quartz: a) intense component, b) weak component.[25]

of vibrations. Consequently, it is apparently incorrect to consider these bands to be analogues. The same ratio of intensities of the considered bands is observed also for glass of the sodium-silicate system, for example for Na-12 glass.

The behavior of the band near 800 cm^{-1} is unique. Its intensity is sufficiently large in fused-quartz spectrum; in two-component glass the intensity diminishes and continues to diminish systematically the richer the glass is in alkali. This band disappears entirely from the spectra of glass that is close to metasilicate in composition. Analogous observations were made by Gross and Kolesova.[46]

The polarization spectrum of fused quartz, shown in Fig. 7, is characterized by a strongly polarized continuous background of Raman scattering, and also by two polarized bands at 495 and 610 cm^{-1} and by depolarized bands near 800, 1130,
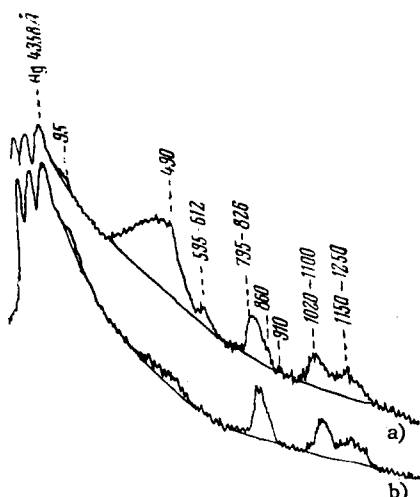

FIG. 8. Photometric curves of polarization spectrum of fused quartz: a) intense component, b) weak component.[49]

and 1230 cm^{-1}. These results are in good agreement with those previously obtained by Harrand.[49] For comparison, we include Harrand's photometric curves in Fig. 8. We note, however, that unlike Harrand's data, no weak polarized satellite of the band near 800 cm^{-1} has been observed in reference 25. This is evidently due to the great width of the spectral interval covered by the photoelectric apparatus of reference 25.

Polarized spectra of two-component silicate glass have much in common with the spectrum of fused quartz. Here, too, we observe a polarized continuous scattering background, a polarized band near 550 cm^{-1}, and a depolarized band near 800 cm^{-1}. In potassium glass a depolarized band is seen near to 250 cm^{-1} in the low-frequency region. The fact that this band is depolarized, along with the above-mentioned absence of noticeable variations in its intensity with the cation content, is convincing refutation of its belonging to vibrations of the K—O bond. It is more likely that this band is related, for example, to deformation vibrations of the silicate skeleton.

There is one important detail in the polarization spectra of all specimens, without exception, namely that the bands of highest frequency ($\sim$ 1096 to 1170 cm^{-1}), which are the "analogues" of the bands near 1130 and 1230 cm^{-1} in fused quartz, are strongly polarized. Comparision of the latest results on the relative intensities of the considered bands with those previously described leaves no doubt that this group of bands, in two-component glass and in fused quartz, is connected with different forms of vibrations. This in turn makes quite doubtful the correctness of the ideas concerning the gradual transition from the fused-quartz structure to that of two-component glass, as developed by Gross and Kolesova.[46, 47] It is apparently more correct to assume that the transition from quartz even to glass with the minimum cation content is accompanied by a radical and thorough structural rearrangement. Were it otherwise, the polarization of the bands could not change in an abrupt manner. Starting with the ideas of gradual structural changes, it is also difficult to imagine that the polarization of the above bands increases in the transition from quartz to glass, because the lattice of glass with defects in the form of disorderly distributed metal cations (the point of view of Gross and Kolesova[46, 47]) is even less regular and symmetrical than the lattice of fused quartz. It will be shown below that a theoretical calculation confirms the conclusions that follow from this experimental investigation.

Also of interest is the behavior of the band near

970 cm^{-1}. In samples of glass containing up to 28 or 30% alkali, this band, being quite weak and diffused, is apparently depolarized. In the bisilicate region ($Na_2O \cdot 2SiO_2$), the band becomes much stronger and pronouncedly polarized. It is hardly possible to explain this essentially-qualitative jump other than to assume a superposition of bands belonging to two different structures, of which one (corresponding to the polarized band) appears in compositions close to the bisilicate. Henceforth, as the alkali content in the glass increases, the new polarized band becomes reinforced even more sharply, becoming the most intense band in the spectrum of potassium metasilicate.

One of the characteristic features of the spectrum of sodium metasilicate is that it is richer in bands as compared with the spectra of glass of the preceding compositions. Polarized light discloses another feature. It turns out that in this case, unlike in the preceding types of glass, the bands with frequencies near 970 and 1070 cm^{-1} are polarized differently: the latter band must be considered depolarized or at least only lightly polarized (Fig. 9).

The spectrum of lead metasilicate differs in many respects from what would appear in the spectrum of the related sodium metasilicate. First, it is simpler than the spectrum of sodium metasilicate. Furthermore, instead of the clearly resolved and intense bands near 970 and 1070 cm^{-1}, which characterize the latter spectrum, we observe here a very broad and intense band with traces of a fine structure and with a maximum near 960 cm^{-1}. It is all completely polarized. In addition, this glass is characterized by an intense continuous Raman scattering, which is entirely absent from the spectrum of sodium metasilicate. All this gives grounds for assuming that the two types of glass the metasilicates of lead and sodium, have substantially different structures.

The measurement data given in reference 25 have been used by the authors to plot the variation of the frequencies of the most intense bands in the spectra of the sodium silicate glass with composition (Fig. 10). Comparing the plot of Fig. 10 with that previously obtained by Vuks and Ioffe (Fig. 1) it is easy to establish their practically complete identity. This also refutes the data (Fig. 3) of Gross and Kolesova[46, 47] given above.

Thus, measurements of frequency and of the degree of depolarization in spectra of sodium-silicate glass are also evidence of a structural rearrangement in the bisilicate region. An analogous conclusion was reached previously by V. A. Florinskaya[50] as the result of an investigation of infrared spectra of these types of glass. It is interesting to
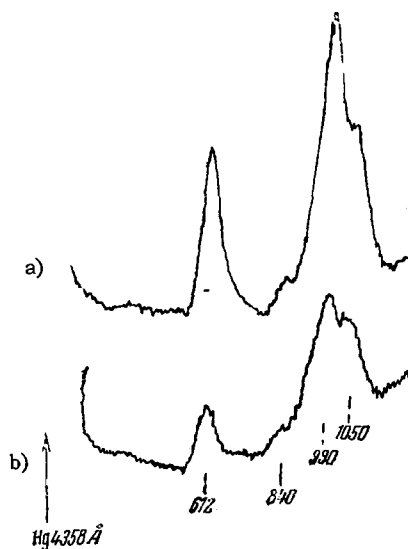

FIG. 9. Photoelectric recording of polarization spectrum of Na-50 (metasilicate) glass: a) intense component, b) weak component.[25]

note that this is also confirmed by certain other measurements, for example by measurements of viscosity of glass.[51] This is why the suggestion by M. F. Vuks that glass contains a chemical compound of sodium bisilicate, corresponding to the layered structure of glass in this region, is probably correct and is undoubtedly worthy of attention.

Conclusions. The most general result of the investigations of Raman spectra of complex silicate glass is a more or less reliable establishment of the fact that the glass contains various large groupings of atoms and anions and, above all, interlinked SiO_4 tetrahedra. There are two points of view concerning the character of the linkage of these tetrahedra in simple alkali-silicate glass. According to the first one, the interlinking of the tetrahedra obeys statistical laws, by virtue of which glass of any composition (with the exception of metasilicate) does not constitute a chemical compound. The authors of the second point of view presuppose the
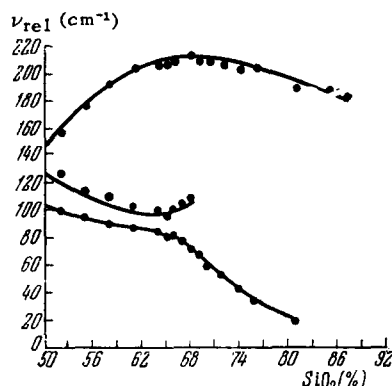

FIG. 10. Dependence of the frequencies of certain bands in sodium-silicate spectra on composition.[25]

structural inhomogeneity of glass, whereby glass of any composition is considered as a superposition of spatial-lattice, layered, and chain-type structural elements. In particular, they assign the chemical formula $Na_2O \cdot 2SiO_2$ to glass of the sodium-bisilicate composition, thus explaining its layered structure.

C. Investigation of the Influence of Different Chemical Elements on the Structure of Silicate Glass [26,27]

The influence of chemical elements on the structure of silicate glass has been the subject of various investigations, but unfortunately by indirect methods as a rule. Much of the work performed and described in the literature is therefore based on purely conjectural, frequently speculative ideas concerning the possible influence of various properties of its component parts on the process of vitrification and, in the final analysis, on the atomic-molecular "architecture" of glass.

There is hardly another physical or physical-chemical method that can give more valuable information on this topic than the method based on the study of the vibrational spectra. Everything discussed in this section has been obtained by means of Raman scattering of light.

We chose[26,27] as objects for our investigations mixed metasilicates of the $NaO \cdot MeO \cdot 2SiO_2$ type and orthosilicates of the $Na_2O \cdot Me_2O_3 \cdot 2SiO_2$ and $2Na_2O \cdot MeO_2 \cdot 2SiO_2$ types, for the case of trivalent and tetravalent Me respectively. The latter, as can be seen, include the oxides of sodium and of various other elements in that total molecular amount at which not a single SiO_4 tetrahedron is bound to another common oxygen atom.

The choice of this composition of glass is far from arbitrary. It is easy to show in this case that to any imaginable structure of glass there can be ascribed definite spectral distinguishing features. Let us consider this problem in detail, using orthosilicates as an example.

Assume that the element Me is present in this glass in the form of cations. Then the spectrum must show the SiO_4 tetrahedra, since the introduction of sodium oxide into the glass, as was shown in references 46 and 25, breaks the Si—O—Si bonds. Only one polarized band in the spectrum corresponds to the case of regular tetrahedra. If the SiO_4 tetrahedra are deformed in the Coulomb field of the cations so strongly that they have lost all their symmetry elements, this is indicated in general by the absence of polarized bands.

In that case when the Me—O bond has an essentially covalent character, we can assume that the oxide of the element Me enters into the general lattice with Na_2O and SiO_2. We expect that this must display a continuous background of polar-

TABLE III. Data on the frequencies and polarizations of bands in spectra of mixed meta and orthosilicate glass[27]

Serial number	Glass	Frequencies (in cm^{-1}) and polarization of the bands
1	$40Na_2O \cdot 10BeO \cdot 50SiO_2$	Cs (sp), 620 (sp), 1065 (pp)
2	$*Na_2O \cdot MgO \cdot 2SiO_2$	Cs (sp), 635 (sp), 1010 (pp)
3	$*Na_2O \cdot CaO \cdot SiO_2$	335 (d), 500 (d), 620 (sp), 985 (pp) 1060 (pp)
4	$*Na_2O \cdot SrO \cdot 2SiO_2$	335 (d), 620 (sp), 980 (pp), 1050 (pp)
5	$*Na_2O \cdot BaO \cdot 2SiO_2$	310 (d), 440–460 (d), 600 (sp), 962 (pp), 1075 (pp)
6	$*Na_2O \cdot ZnO \cdot 2SiO_2$	Cs (sp), 625 (sp), 1045 (pp)
7	$*Na_2O \cdot CdO \cdot 2SiO_2$	Cs with boundary at 475–540 (sp), 625 (sp), 985 (pp)
8	$*Na_2O \cdot PbO \cdot 2SiO_2$	Cs with boundary at ~530 (sp), 650 (pp), 962 (pp)
9	$40Na_2O \cdot 10Al_2O_3 \cdot 50SiO_2$	Cs with boundary at ~565 (sp), 1065 (pp)
10	$**Na_2O \cdot Bi_2O_3 \cdot 2SiO_2$	Cs with boundary at ~445 (sp), 980 (pp)
11	$**Na_2O \cdot B_2O_3 \cdot 2SiO_2$	Cs with boundary at ~510 (sp), 630 (sp), 730 (?), 1067 (pp)
12	$**Na_2O \cdot TiO_2 \cdot 2SiO_2$	Cs with boundary at ~300 (sp), broad band at 345 (d), 700 (sp), 875 (sp), 1015 (d)
13	$**2Na_2O \cdot GeO_2 \cdot 2SiO_2$	295 (d), 580 (sp), 855 (pp), 965 (pp), 1092 (pp)
14	$40Na_2O \cdot 10ZrO_2 \cdot 50SiO_2$	Cs (sp), 605 (sp), 930 (pp), 1075 (pp)
15	$**2PbO \cdot SiO_2$	Cs (sp), with boundary at ~500, 925 (pp)

Symbols: sp — strongly polarized, pp — partially polarized, d — depolarized, cs — continous scattering.

Note: Glass marked with one or two asterisks has (by analysis) a composition quite close to meta- and ortho-silicate, respectively. All other types of glass have not been analyzed and their composition is assumed to be in accordance with their synthesis.
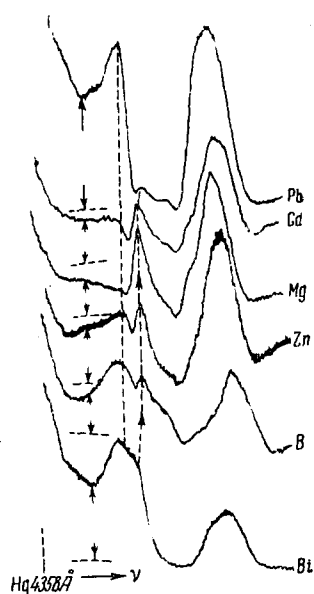
FIG. 11. Photoelectric recordings of spectra of several mixed meta-and ortho-silicate types of glass. The dashed line shows the level of the background near the exciting line, and the arrows indicate the continuous scattering. [26,27]

FIG. 12. Photoelectric recording of polarization spectrum of mixed metasilicate glass, containing PbO as the third component: a) intense component, b) weak component. [26,27]

ized Raman scattering adjacent to the exciting line, analogous to the scattering in fused quartz and in two-component alkali-poor glass, i.e., with strongly-developed spatial linking of the tetrahedra.[25] It will be shown below that this is fully confirmed experimentally. In addition, the bands of the spectra will probably be particularly broad in this case.

It is not excluded, for example, that the oxides of the element Me, particularly if they are glass-forming themselves, will not enter at all into the common lattice, and will more likely tend to form their own lattice. A superposition of the spectra of the glass-forming oxide and of the metasilicate $Na_2O:SiO_2$ must then be observed. The latter has been thoroughly investigated by us experimentally[24,25] and by B.I. Stepanov and A. M. Prima[52-55] theoretically, and has a sufficiently characteristic form. Naturally, intermediate structures are also possible. The spectra of metasilicate glass can be interpreted in approximately the same manner.

In references 26 and 27 we reported on a study of the influence of all the most important readily-available elements (Be, Mg, Ca, Ba, Si, Zn, Cd, Pb, Al, Bi, B, Ti, Ge, Zr). Three of these—Be, Al and Zr—were investigated in glass somewhat different from that described above (with a lower relative content of oxides of these elements). It was possible to produce and investigate lead glass in the form of a simple orthosilicate $2PbO \cdot SiO_2$.

Even the results of the investigation of lead orthosilicate show that the character of its spectrum is actually compatible with the assumption of the existence of a spatial lattice made up of SiO_4 tetrahedra, linked to each other by the lead atoms. It is remarkable that the spectrum of lead
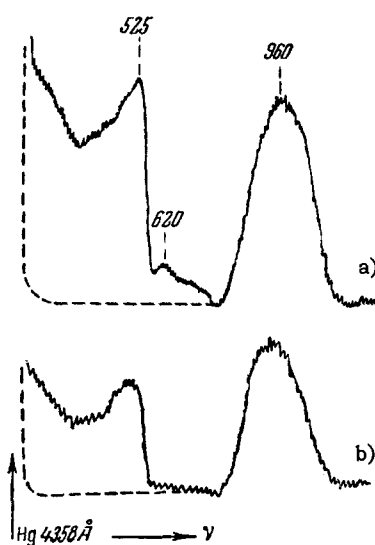
metasilicate, as already noted, also exhibits features of such links, manifesting itself in particular in the presence of a continuous background of polarized Raman scattering. It must therefore be assumed that in this glass all the tetrahedra are linked, at least partially, through the lead atoms.

Further investigation of the above-mentioned mixed meta and ortho-silicates has made it possible to subdivide all elements into three groups, in accordance with their effects on the character of the spectra.

Table III lists the measured frequencies in spectra of various types of glass. Spectra of certain representatives of the first group, the most extensive one, are shown in Fig. 11. The polarization spectrum of one type of glass of this group is shown in Fig. 12. These spectra are characterized by a more or less intense continuous background of polarized scattering, with a small peak near its boundary. This peak retains its position (near 625 cm^{-1}) approximately in all glass types of this group. The spectra also contain very broad high-frequency bands with a maximum near 980 cm^{-1}. The widths of the bands, and particularly the presence of a continuous scattering background, shows convincingly in our opinion, a partial spatial linkage of most SiO_4 tetrahedra via the Me atoms. Aluminum, bismuth, lead, and boron have a particularly strong tendency to penetrate the structural glass lattice. Judging from the presence of a band near 625 cm^{-1} which is characteristic of the metasilicate,[46,25] it appears that a small portion of the Na_2O and SiO_2 molecules, which do not enter into a common lattice with the element Me, forms structures that are close to metasilicate chains. The number of chain structures differs with different types of glass. A more or less stronger tendency to enter
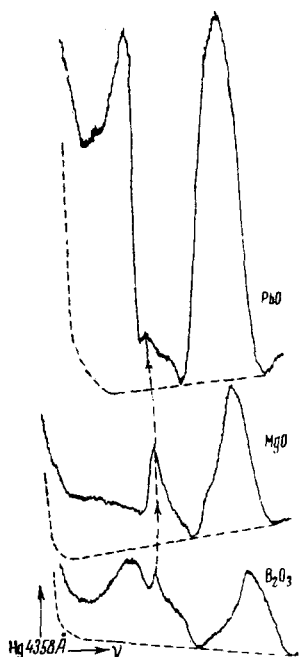
FIG. 13. Comparison of the spectra of glass containing PbO, MgO, and B_2O_3. The spectra have been recorded under identical conditions.[27]

FIG. 14. Photoelectric recording of spectra of mixed metasilicate glass, containing CaO, BaO, and SrO.[26,27]

into the structural glass lattice is displayed also by beryllium, magnesium, zinc, cadmium and zirconium.

When discussing the problem of the tendency of chemical elements to enter into the general structural lattice, we must not lose sight of the following. The intensity of the Raman spectra, as noted earlier, is directly related to the character of the bonds. The more covalent the bonds, the more intense the spectra, in general. Consequently, operating with intensities in the scattering spectrum, we are essentially speaking, characterizing the "covalent contribution" of the chemical element in the structural lattice. This is why an estimate of the tendency of the chemical elements to enter into the structural lattice should be made taking into account the general intensity of the spectrum.

In connection with this, it is of undoubted interest to compare spectra obtained under perfectly identical conditions, of different types of glass. In view of the fact that many specimens were different in dimensions and quality, we could make this comparison[26, 27] only for three types of glass, containing PbO, MgO, and B_2O_3. The spectra are shown for comparison in Fig. 13. We see that the most intense spectrum is that of lead glass, and the less intense is that of boron glass. The magnesium glass occupies an intermediate place.

One might think that the high intensity of the spectrum of lead glass, lightly tinted yellow, is due to the relative nearness of the exciting line (λ = 4358Å) to the corresponding absorption band (resonance phenomenon). This doubt is

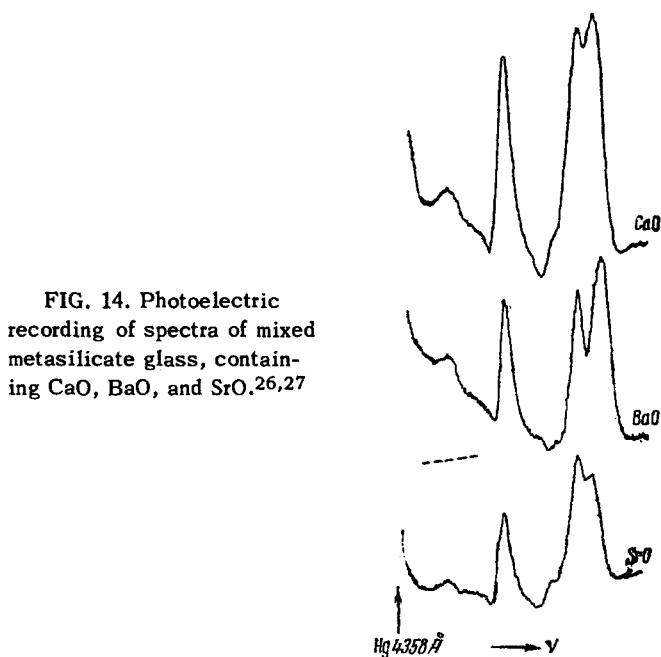however completely dispelled in the case of uncolored magnesium glass. Apparently, it is the degree of covalence of the Me—O bonds which manifests itself. This means that the Mg—O bond in the glass is more covalent than the B—O bond.

At first glance this conclusion is paradoxical. Calculation of the degree of ionization of the bonds, using the electro-negative potential scale of Pauling, gives the opposite results (see Table I). One must note, however, that this scale is, strictly speaking, applicable only to isolated bonds. In such a complex condensed system as glass, the situation may change.

In our opinion, a convincing illustration of this fact is germanium glass GeO_2. The results of the investigation of certain types of germanium-containing glass will be reported below. We note here only that its spectrum is several times more intense than the spectrum of glass-forming silicon, although both types of glass have structures which are identical in all respects. In addition, according to calculations, the Ge—O bonds and the Se—O bonds have an equal degree of covalence which amounts to approximately 50%.

Thus, estimates of the degree of ionization (covalence) of the bonds in glass, based on the use of the ordinary scale of electro-negative potential of the elements, have a roughly approximate character and do not take into account the mutual influence between the different structural formations in the glass. We note that similar considerations have already been stated in the literature.[11]
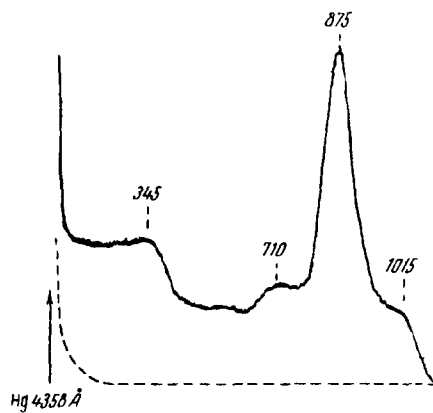
The second group, according to spectroscopic

FIG. 15. Photoelectric recording of the spectrum of the glass $2Na_2O \cdot TiO_2 \cdot 2SiO_2$. The dashed line shows the level of the background.[27]

FIG. 16. Photoelectric recording of the polarization spectrum of the glass $2Na_2O \cdot TiO_2 \cdot 2SiO_2$: a) intense component, b) weak component.[27]

investigations, includes the glass types that contain CaO, BaO, and SrO. Their spectra are shown in Fig. 14. They are characterized by somewhat narrower bands, by the absence of a continuous background of polarized scattering (instead of which we see two comparatively weak depolarized maxima, ~ 320 and ~ 470 cm^{-1}), by a well resolved structure of the high frequency band, and by somewhat different intensity distributions. In their appearance and in all details, with the exception of the maxima at the ~ 320 and 470 cm^{-1}, all the spectra obtained recall those of the sodium-silicate glass, which is close in composition to the meta-silicate. The similarity is particularly pronounced in the case of glass containing SrO.

Since these types of glass are metasilicates with respect to their total content of Na_2O and MeO, the facts noted above lead to the conclusion that the metals Ca, Ba, and Sr enter into the glass in the form of cations (like Na and K), and consequently the spectra of these types of glass manifest vibrations of the silicon-oxygen metasilicate chains.

The third group contains only one single type of glass with composition $2Na_2O \cdot TiO_2 \cdot 2SiO_2$. The spectrum of this glass, shown in Fig. 15, is most unique. Unlike the preceding spectra, the bands near 625 and 980 cm^{-1} have disappeared from this spectrum. They are replaced by a very intense and polarized band near 875 cm^{-1} (see Fig. 16). Furthermore, the spectrum also displays a continuous background of polarized scattering with a strongly shifted boundary (apparently to approximately 750 to 800 cm^{-1}). Pronounced against the background of this scattering are a depolarized band (with boundary near 345 cm^{-1}) and a polarized band (near 700 cm^{-1}). Adjacent on the high-frequency side to the band near 875 cm^{-1} is a weak depolarized satellite with a frequency of 1015 cm^{-1}.

The impression is gained that in this case

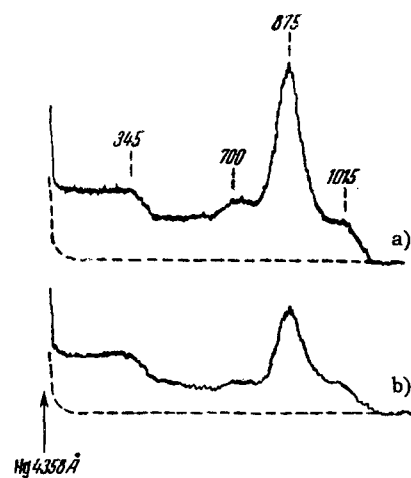weak vibrations of the free SiO_4 tetrahedra and of the complex spatial lattice $SiO_2 \cdot TiO_2$ appear in the spectrum. In this connection, the band near 875 cm^{-1} is interpreted by us[26,27] as belonging to the completely symmetrical vibration of the SiO_4 tetrahedra. The 1015 cm^{-1} band is ascribed to one of the triply-degenerate anti-symmetrical vibrations, and the very broad band with a high-frequency boundary at nearly 345 cm^{-1} is attributed to another triply-degenerate and to a doubly-degenerate vibration. This interpretation of the bands of the tetrahedron vibrations is confirmed by theoretical calculations.[52-55] It is also in good agreement with the results of an investigation on a large number of other tetrahedral molecules[56] and with data on polarization measurements.[26,27]

Another fact worthy of attention is that the boundary of the continuous scattering background in titanium glass, unlike that in other silicate glass, shifts sharply towards the higher frequencies. To explain this shift (with allowance for the opposing effect of the mass of the titanium atom), it is necessary to assume that the Ti—O bond is considerably more rigid than the Si—O bond. It is not excluded that the strengthening of the Ti—O bond is due to the three d-electrons, which are the external electrons of the titanium atom and which participate in the formation of the bond.

For the sake of clarity, Figs. 17 to 19 show schematically the structures of several types of glass as derived from the analysis of the spectroscopic data.

It is of interest to compare the conclusions concerning the tendency of different elements to enter into the structural lattice drawn from spectroscopic investigations and from other investigations. It is commonly accepted that aluminum has
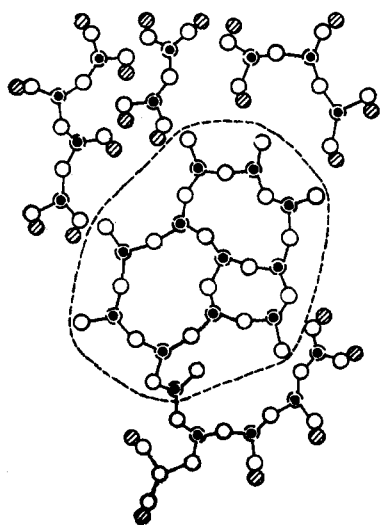
FIG. 17. Schematic representation of the structure of two-component alkali-silicate glass. Symbols: o) O, ☉) Si, ●) Na. The dashed line separates the spatial lattice region. Outside the dashed region are traces of layers made of SiO$_4$ tetrahedra.[26,27]

a very pronounced such tendency. Data on Raman spectra, as already noted above, confirm this fully. The results of the investigation of the thermal expansion of various types of glass, made by Stanworth,[57] are compatible with the assumption that magnesium and zinc can enter into the structural lattice, while calcium and barium cannot. These facts are also in good agreement with the spectroscopic data. According to Fajans and Kreidl,[58] and also according to a later paper by Stanworth,[60] the tendency to enter into the structural lattice is a characteristic of lead and bismuth atoms. Recently it has even been possible to melt "silicate" glass with the total molecular content of Bi$_2$O$_3$ and PbO reaching 95%.[60] Such types of glass essentially
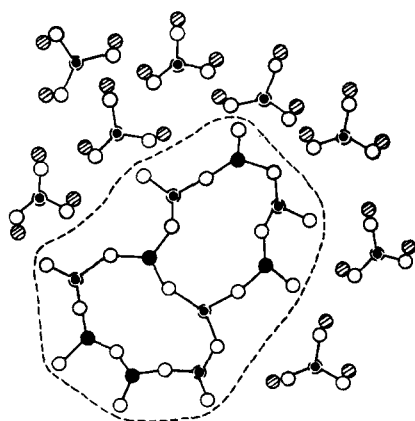

FIG. 19. Schematic representation of the structure of a three-component glass containing TiO$_2$ as a third component. Symbols: o) O, ●) Si, ☉) Ti, ●) Na. The dashed line separates the spatial-lattice region composed of SiO$_4$ and TiO$_4$ tetrahedra. Outside the dashed region are the free SiO$_4$ tetrahedra.[26,27]

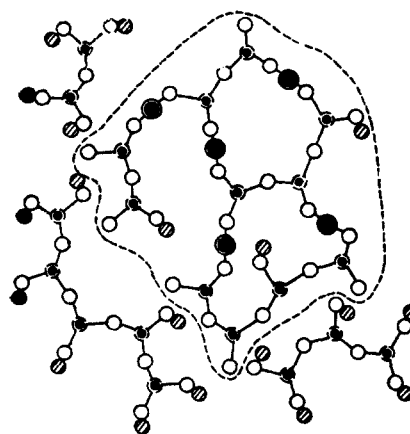FIG. 18. Schematic representation of the structure of three-component glass containing PbO as a third component. Symbols: o) O, ●) Si, ☉) Pb. The dashed line separates the spatial-lattice region in which the SiO$_2$ tetrahedra are partially bound through the lead atoms. Chains of SiO$_4$ are shown outside the dashed region.[26,27]

cannot even be called silicate glass. These facts are also in good agreement with the results of the investigation of the Raman spectra.

Thus, the interpretation we have proposed[26, 27] for the Raman spectra of mixed meta- and ortho-silicates, can be considered as fully acceptable and can serve as a basis for further experimental investigations of similar type.

It is also of interest to compare the results of spectroscopic investigation with the conclusions concerning the structure of various types of glass, formulated by Dietzel.[7, 8] We recall that according to Dietzel the "strong cations" (such as B^{+3}, Bi^{+3}, Ti^{+4}, Ge^{+4} etc.) should not show a strong tendency to enter the silicon-oxygen lattice, but should tend, on the contrary, to produce their own surroundings of oxygen anions.* In this sense they compete with the cations of silicon. Spectroscopic data, at least for those types of glass investigated in references 26 and 27, do not confirm this conclusion fully. The picture obtained is much more complicated than that which follows from Dietzel's conjectures.

Let us examine this problem in somewhat greater detail.

According to Dietzel, there should exist in three-component sodium-borosilicate glass isolated boron-oxygen and silicon-oxygen lattices with uniformly distributed sodium cations. The glass we investigated had (according to analysis) the composition of an orthosilicate, Na$_2$O.B$_2$O$_3$.2SiO$_2$. Consequently, the oxygen atoms of the silicon-oxygen lattice should be surrounded by twice as many Na$^+$

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*Again we recall that according to Dietzel the tendency towards formation of a general structural lattice is completely determined by the electrostatic interaction forces.

cations as the oxygen atoms of the boron-oxygen lattice. If this is so, the spectrum should contain a superposition of the vibrations of Na-25 borate and silicate glasses.

Fig. 20 shows, along with the spectrum of the three-component glass, the spectra of the two-component glasses Na-20 (silicate) and Na-20 (borate). The small variation in the compositions of these types of glass is insignificant. As can be seen, no superposition of the spectra is observed. Consequently, the Dietzel rule is not obeyed in this case.

Matters are even worse with titanium glass. Here, as already noted, it is reasonable to assume the existence of a complex lattice of the $SiO_2.TiO_2$ type and of free tetrahedra, in which the negative charges of the oxygen atoms are compensated by the charges of the sodium cations. Yet, according to Dietzel, the spectrum should have displayed at least the bands of glass having the Na-40 composition.

Neither does Dietzel's theory allow for the behavior of such metals as bismuth, lead, cadmium, zinc, and several others. This is particularly clearly seen in the case of glass containing Bi_2O_3. No features of the Na-25 composition are observed in the spectrum of this glass (see Fig. 11).

An example where the Dietzel rules are exactly obeyed is the mixed orthosilicate of germanium, $2Na_2O.GeO_2.2SiO_2$, the spectrum of which is shown in Fig. 21. From the requirement of uniform distribution of sodium cations (the Dietzel concept) it follows that the spectrum of this orthosilicate should display the bands of the Na-40 two-component silicate and germanium glasses. This is indeed observed experimentally, as shown directly for the first of the two types of glass by Fig. 21. Thus, an analysis of the spectroscopic data makes it possible to refine and to correct the widespread ideas concerning the structure of glass.

In connection with the foregoing material, we also comment on certain incorrect, but widely held interpretations of the infrared spectra of various crystalline silicates.

It is known that silicates can exist in the form of various structures. Some of these form a spatial lattice. A typical representative of such silicates is quartz. Others form layers and chains. There are, finally, silicates to which one ascribes the so-called "island" structure. These are crystalline analogues of orthosilicate glass. Schafer, Matossi, and Wirz[41] have investigated, among others, the infrared spectra of silicates with "island" structure: Be_2SiO_4—phenacite, (CaOTi) SiO_4—titanite, (Zn, Mg) SiO_4—troostite,
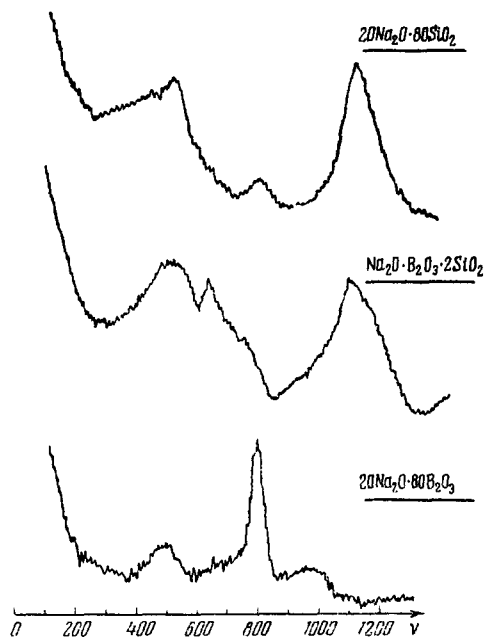
FIG. 20. Comparison of spectra of mixed orthosilicate $Na_2O.B_2O_3.2SiO_2$, Na-20, silicate glass, and Na-20 borate glass.

and others. This reference also cites literature data on zircon $ZrSiO_4$ and willemite Zn_2SiO_4. The analysis of the spectra has made it possible for the authors of reference 41 to attribute four bands belonging to these silicates to vibrations of the free tetrahedra of SiO_4. These data are then used to interpret the vibrational spectra of glass.

As follows from the results of even a roughly approximate study of Raman scattering, no free tetrahedra of SiO_4 appear in orthosilicate glass. Consequently, the identification of the corresponding bands in the spectra of crystalline silicates, as proposed by Schafer, Matossi and Wirz, is not convincing.

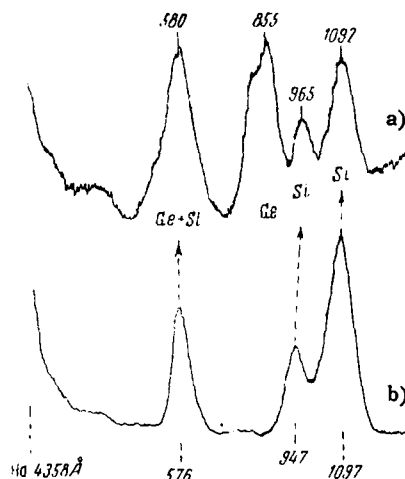We confine ourselves for the present to the

FIG. 21. Comparison of spectra of the mixed orthosilicate $2Na_2O.GeO_2.2SiO_2$ (a) and Na-40 silicate glass (b).

description of the character of the spectra of various types of glass and to an interpretation of their structure. It is difficult to explain at this stage the different behavior of the chemical elements without additional experimental material. In particular, it is exceedingly important and interesting to carry out analogous investigations on other systems, for example phosphate and borate. To show how difficult and involved is the problem of the influence of chemical elements on the structure of glass, we call attention again to certain of the types of glass investigated in references 26 and 27. As already noted, the oxides of titanium and germanium influence differently the structure of three-component glass. Yet titanium and germanium have identical valence and do not differ greatly in the values of the ionic radii. Boron and bismuth, on the other hand, have substantially different ionic radii, but apparently behave in glass in an analogous manner.

Conclusions. The investigation of Raman spectra of mixed meta and orthosilicates indicates the diverse roles of the chemical elements in the vitrification process. The spectra are separated into three groups by their character. Each spectrum is amenable to a definite interpretation and leads to conclusions on the structure of the investigated glass. There is full agreement between the behavior of the chemical elements as established by spectroscopic means and by other indirect methods.

D. Spectra of Liquid Silicates (Orthosilicic-Acid Ethers Considered as Analogues of Silicate Glass

More than 20 years ago Singer and Weiler[61] and Singer[62] undertook to interpret spectra of certain silicates and silicate glass on the basis of an experimental study of liquid silicates (orthosilicane ethers), i.e., compounds having a general formula Si $(OC_mH_n)_4$. Recently an analogous attempt was repeated by A. N. Lazarev.[63] The importance of such comparisons is as follows. As already noted, the principal structural element in glass is the SiO_4 tetrahedron. According to x-ray structural investigations of monomeric methyl ether $Si(OCH_3)_4$, carried out by Eulitz,[64] a SiO_4 group appears in the substance, with the same symmetry and the same dimensions as in the crystalline quartz. Thus, by studying the vibrational spectra of the monomeric ether and its condensation products it would appear possible to separate the frequencies of the internal vibrations of the SiO_4 tetrahedron and follow their variation as a function of the degree of polymerization of the $Si(OCH_3)_4$

molecules and then apply the data obtained to the interpretation of the spectra of glass.

This, indeed, is the procedure followed in references 61 and 62. Analyzing their own experimental data, they found it possible to ascribe to the vibrations of the SiO_4 tetrahedral group in the spectrum of monomeric methyl ether the following frequencies (in cm^{-1}): 1205, 1192, 1170 (ν_1), 1110-1080 (ν_2), 842 (ν_3), and 642 (ν_4). Since the vibrations ν_1 and ν_2 are three-fold degenerate, their splitting into several components, in the opinion of Singer and Weiler, just implies the removal of the degeneracy. According to Weiler[62] the polarization measurements do not contradict the proposed interpretation.

As the degree of polymerization of the ethers increases (upon transition from the monomeric to the dimeric, trimeric and decameric ether) the bands ν_1 and ν_2 practically retain their position in the spectrum while the bands ν_3 and ν_4 shift towards lower vibration frequencies (this is particularly true of the latter, which reaches rapidly a limiting value of approximately 520 cm^{-1}). The limiting values of the frequencies in the spectrum of the investigated ethers are compared by Singer and Weiler with the frequencies of the bands in the spectrum of crystalline quartz.

A. N. Lazarev's investigation[63] of methyl and ethyl ethers of silicate acids are based on similar considerations. The difference consists only in that the treatment of the results obtained is somewhat different: Lazarev compares the limiting values of the frequencies of the silicon skeleton of the ethers with the frequencies of alkali-silicate glass, having a composition close to that of the metasilicate, and made up of infinitely long silicon-oxygen chains, rather than using Weiler's comparison with the frequencies of crystallne quartz. Lazarev establishes here an almost complete correspondence between the spectra of both objects.

We doubt seriously that the spectra of monomeric ethers of silicic acid can display discrete vibrations of the SiO_4 tetrahedra. It is much more correct to propose the possibility of interaction between the vibrations of the Si—O and C—O bonds. In the interpretation of the bands it then becomes necessary to take into account a different, lower than Td, symmetry of the ether molecule as a whole. A solution of the mechanical problem of the vibrations of the $Si(OCH_3)_4$ molecules, carried out by Iguchi,[65] has shown that in this case four polarized bands should appear in a spectrum among the skeleton vibrations.

In order to verify this premise, Lazarev, Tulub, et al.[66] undertook a thorough investigation of the

TABLE IV. Data on the frequencies, intensities, and polarizations
of bands in spectra of different silicane ethers[66]

$Si(OCH_3)_4$	$OSi_2(OCH_3)_6$	$Si(OC_2H_5)_4$	$OSi_2(OC_2H_5)_6$	$O_2Si_3(OC_2H_5)_8$
412 (1; 0.80)	445 (1.5;) 577 (10; 0.05)		614 (2; 0.13)	604 (1.5; 0.18) 640 (0)
640 (10; 0.03)	692 (0)	656 (6; 0.05)	685 (0)	703 (0.5; ?)
844 (2; 0.80)	808/838 (5.5; 0.50)	792/822 (3; 0.62)	800 (1.5; 0.31)	796 (2; 0.34)
1082/1111 (5; 0.20)	1090/1126 (6; 0.40)	939 (3; 0.53) 1096 (8; 0.27)	935 (1; 0.78) 1095 (2.5; 0.27)	940 (1; 0.80) 1096 (2.5; 0.22)
1186 (4; 0.32)	1190 (4.5; 0.30)	1173 (4.5; 0.15)	1170 (0)	1170 (0)
1269 (1.5; pol.)	1267 (2; pol.)	1205 (2; 0.74) 1302 (4.5; 0.77)	1296 (1.5; 0.70)	1295 (2; 0.48)
1371 (1; pol.) 1466 (5.5; 0.80)	1375 (1; pol.) 1466 (8; 0.80)	1460 (10; 0.83)	1456 (4; 0.70)	1456 (4; 0.55)

Symbols: The first number in the parenthesis indicates the relative intensity of the band, the second its degree of depolarization. Weak lines, observed photographically, are assigned everywhere a zero intensity value.

polarization spectra of monomeric methyl and ethyl ethers, and also of certain condensation products of these ethers. The degrees of depolarization were measured by the photoelectric method. The data obtained are listed in Table IV, and some of the recordings are shown in Fig. 22.

We see that the spectrum of methyl ether, in contradiction with Weiler's experimental data,[62] contains not one but several polarized lines. This is in good agreement with the theoretical calculations of Iguchi.[65] An approximately analogous picture is observed in the case of other ethers. This proves that the four bands in the spectrum of the $Si(OCH_3)_4$ molecules cannot be attributed to vibrations of SiO_4 tetrahedra and raises in general serious doubts concerning the possibility and advisability of the very attempts of paralleling the spectra of silicane ethers and those of silicate glass for the purpose of determining the structure of glass.

3. THEORETICAL INTERPRETATION OF RAMAN SPECTRA OF CERTAIN CRYSTALS. COMPARISON WITH EXPERIMENTAL DATA FOR SILICATE AND GERMANIUM GLASS

Attempts at a theoretical interpretation of vibrational spectra of crystalline silicates have been undertaken many times. Thus, for example, Saksena[67] calculated the frequencies in the spectrum of α-quartz, and Barriol[68] did the same for β-quartz. These calculations, however, are rough and the results are presented in a very inconvenient form, which makes comparison with experiment difficult. Matossi[69] derives expressions for the vibration frequencies of the pyroxene chain of SiO_4 tetrahedra, of tetrahedra linked in pairs, and of quartz. It is

difficult to judge the accuracy of these expressions. We can only say that, in particular for the pyroxene chain, they are known to be incorrect, since Matossi employs incorrect values for the cosine of the Si—O—Si angles.

The application of the results of calculations of the spectra of crystalline silicates to the case of glass is fraught with certain specific difficulties. It is necessary to know how the tetrahedra are linked with each other in the glass and what role is played by various chemical elements in the structure of the glass. Direct experiment cannot answer the first question. It is more correct to seek a confirmation in the results of the theoretical calculations of the frequencies, based on a sufficiently reasonable structural model. The different views
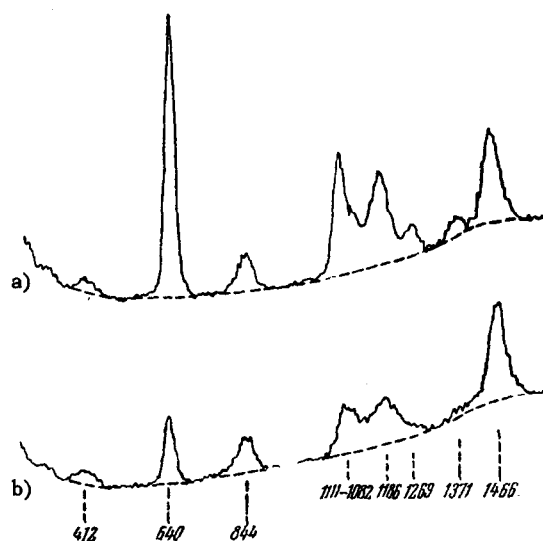

FIG. 22. Photoelectric recording of the polarization spectrum of $Si(OCH_3)_4$: a) intense component; b) weak component.[66]

on the character of the linkages between the SiO_4 tetrahedra in alkali-silicate glass have already been discussed.

The situation is somewhat simpler when it comes to the influence of chemical elements on the structure of the glass. The available experimental data make it possible to judge quite reliably what elements are involved and to what extent they enter into the silicon-oxygen lattice of the glass.[26, 27] This in turn determines the applicability of the theoretical calculations and points the way to further refinement of these calculations.

Until recently there were practically no investigations in which the results of the theoretical calculations of the frequencies in the spectra of crystalline silicates were used to determine the structure of glass. The only attempt of this kind was made by Bobovich, Girin et al.[21] These authors presuppose the existence of lattice structures, layer structures, and chain structures in alkali-silicate glass. Applying the expressions derived by Matossi[69] for the vibrations of a chain to certain bands in the spectrum, they succeed in interpreting many important experimental facts. Nevertheless the results obtained are far from conclusive, since the expressions for the frequency are themselves doubtful.

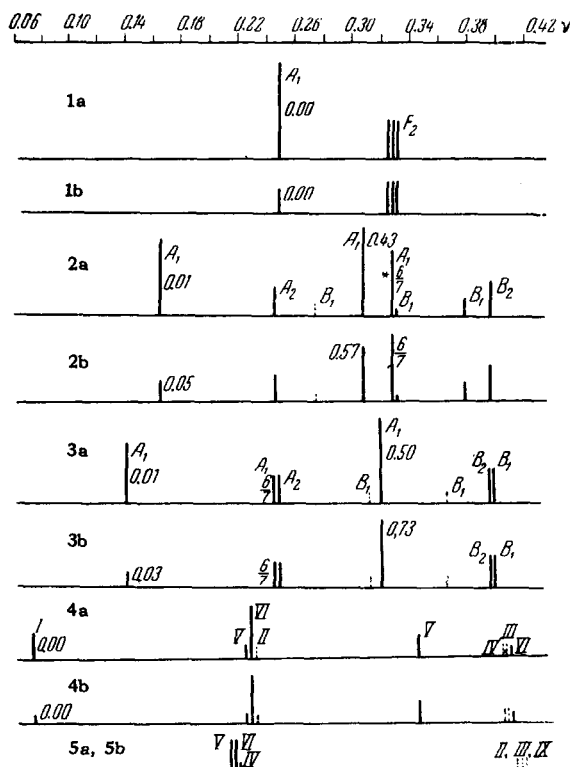Only the insufficient development of the theory

FIG. 23. Theoretical Raman spectra: 1) SiO_4 tetrahedron, 2) chain, 3) layer, 4) β-quartz, 5) β-cristobalite; a) with $\partial\alpha_{\parallel}/\partial q = 0$, b) with $\partial\alpha_{\perp}/\partial q = 0$ (references 52-55).

of the problem can explain the fact that for a long time the authors of many papers[70-74] have guided themselves in the interpretation of experimental data by the definitely incorrect hypothesis, first stated by Schafer, Matossi and Wirtz,[41] that the spectra of glass retain the vibration forms of isolated SiO_4 tetrahedra. To some extent this problem has been treated by us earlier. A correct critique of the hypotheses of Schafer, Matossi and Wirtz and of their successors is contained in the work by V. A. Kolesova.[75]

A very important step forward in the interpretation of the vibrational spectra of crystalline silicates and of glass was taken recently by B. I. Stepanov and A. M. Prim.[52-55] They have considered the vibrations of β-quartz and of cristobalite, free SiO_4 tetrahedra, the pyroxene chain, and an infinite layer of SiO_4 tetrahedra. The last case was analyzed first. All the calculations were made in two versions, a rigorous one and one with reasonable simplifications, using a method previously developed by M. A. El'yashevich and B. I. Stepanov as applied to vibrations of molecules. In addition to the frequencies, they also calculated the relative intensities of the vibrational bands, and also the states of polarization of Raman bands. For this purpose they used an additivity scheme, proposed by M. V. Vol'kenshtein, and took into account the variations in the polarizability components in direction of and transverse to the bonds.

Without going into details, let us list the principal results of the simplified version of the calculations, when the effect of the deformation vibrations is excluded. In all cases, with the exception of quartz and cristobalites, two elastic constants are introduced. These results are then compared with the experimental material.

For convenience, some of these results, pertaining only to Raman spectra, are gathered in the form shown schematically in Fig. 23. The following conventional notation is used. The dotted lines indicate the bands that are forbidden in the used approximation, while double lines signify the natural bands. The letters A, B, and F with indices and Roman numbers indicate the type of symmetry of the vibrations, while the numbers represent the states of polarization of the bands. The vibrations denoted by A_2, B_1, B_2 and F, as well as by V and VI, are depolarized. The relative intensities of the Raman bands depend strongly on the ratio of the quantities $\partial\alpha_{\perp}/\partial q$ and $\partial\alpha_{\parallel}/\partial q$. Figure 23 shows the results of calculations for two extreme cases: $\partial\alpha_{\perp}/\partial q = 0$, $\partial\alpha_{\parallel}/\partial q \neq 0$ and $\partial\alpha_{\perp}/\partial q \neq 0$, $\partial\alpha_{\parallel}/\partial q = 0$. When $\alpha_{\perp}/\partial q = \partial\alpha_{\parallel}/\partial q$, the selection rules allow only the fully-symmetric vibrations. As

follows from the available experimental data for crystals, it is apparently the intermediate case that is realized in practice. The asterisks indicate the random degenerate vibrations, for which the degeneracy is removed if the different Si—O bonds are characterized by two elastic constants of different values.

It is seen from Fig. 23 that each investigated structure is characterized by a specific spectrum. In particular, in quartz and cristobalite, unlike in the chain and in the layer, the depolarized bands lie in the region of the highest vibration frequencies. The spectrum of β-cristobalites appears simpler than the spectrum of β-quartz; this, of course, is caused by its greater symmetry. One might think that this feature alone could identify the particular structure. Unfortunately, the lack of sufficient experimental material does not for the time being permit a consistent verification of the theoretical results for crystals. We note, however, that the data contained in reference 76 appear not to confirm the relative simplicity of the spectrum of β-cristobalite.

To compare the above schematic spectra of crystalline silicates with real spectra of glass it is necessary, as already noted, to make a definite assumption concerning the structure of glass. Stepanov and Prima[52-55] started out with the assumption that fused quartz, sodium bisilicate, and sodium metasilicate represent, as regards structure, arbitrarily oriented minute crystals of quartz and two-dimensional and undimensional silicate crystals, respectively. This has made it possible to calculate the intensities and the degree of depolarization of the bands, using the same rules as apply in the case of ordinary systems with freely oriented particles.

Naturally, the model chosen for glass is too primitive from the physical point of view. If we start out with the crystalline concepts, it is more correct, in any case, to have the term crystallite signify a near-order region that has no phase boundaries, a fact to which we have already called attention. The choice on the part of Stepanov and Prima[52-55] is justified, however, by considerations of simplicity of calculation. A refinement of the glass model, in the sense formulated above, could hardly add anything new to the results of the calculations.

Attention must be called to still another circumstance. Strictly speaking, the experimental data, at least for fused quartz, should be properly compared with the theoretical ones for β-quartz and not for α-quartz, which is a quartz modification that is stable in the region of ordinary tempera-
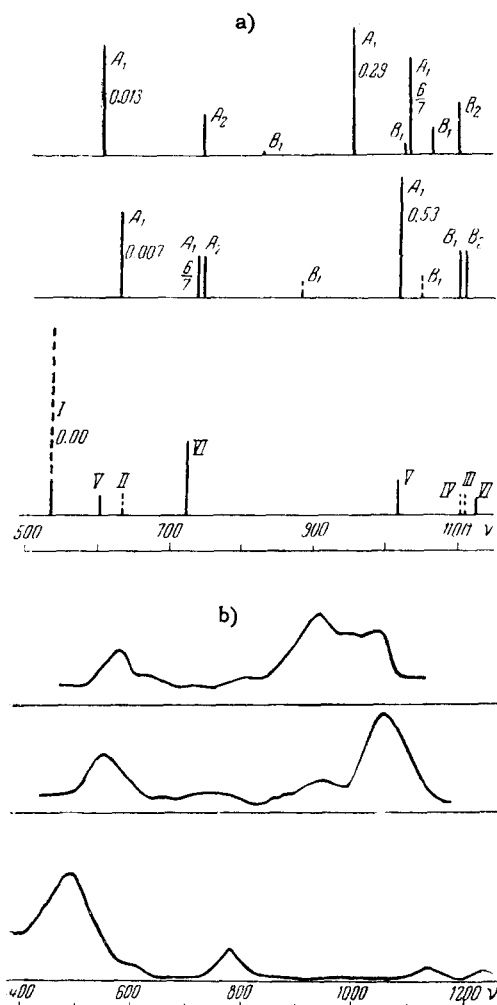

FIG. 24.Theoretical (a) and experimental (b) Raman spectra of various types of glass (upper row— metasilicate glass, middle row — bisilicate glass, lower row — fused quartz).[52-55]

tures. Stepanov and Prima[52-55] did not carry out the corresponding calculations. One can expect, however,[77,78] that allowance for this circumstance will not introduce substantial corrections. In any case, the corrections will not exceed the errors associated with the approximate character of the calculations. Having made these remarks, let us turn to a comparison of the theoretical and experimental data on the spectra of glass.

As we did previously, we now present the results of the calculations schematically, showing alongside, also in schematic form, the experimentally-obtained spectra (Fig. 24). In the calculations we have assumed for the elastic constants values that give their best agreement with the experimental data for sodium metasilicate.[25] In addition, for components of the polarizability in direction of and transverse to the bonds, we assumed the relation $\partial \alpha_\perp / \partial q = 1/4 \, \partial \alpha_\parallel / \partial q$, which is frequently satisfied in vibrations of different molecules.

As can be seen from Fig. 24, the calculated and observed spectra are in agreement with respect to all the substantial features. We note above all that results of calculations and their comparison with experimental data do not contradict the hypothesis of the layered structure of glass with the composition of sodium bisilicate ($Na_2O.2SiO_2$). To obtain additional proof of the correctness of this hypothesis, we have applied elsewhere[79] the results of the theoretical calculations of Stepanov and Prim to the spectrum of sodium bigermanate ($Na_2O.2GeO_2$). In addition, we took into account very close analogy in the structure of the crystalline germanium dioxide and that of α-quartz, thanks to which the silicate and germanium glass can be considered as formed by isotopic oxides of the same type. The frequencies of the spectrum of sodium bigermanate, calculated on this basis, are in good agreement with the observed ones. This proves the existence of the layered structure of sodium bisilicate, inasmuch as the equations for the vibrations used in the calculations were indeed derived under the assumption of a layered linkage of the SiO_4 tetrahedra.

Another fact deserving of attention is that, according to calculation, the spectrum of fused quartz, unlike the bisilicate spectrum, to which a layered structure is ascribed, contains a low-intensity depolarized vibration, V, in the region of approximately 1050 to 1200 cm^{-1}. Conse-

FIG. 25. Photoelectric recordings of spectra: a) crystalline quartz, b) fused quartz. The latter specimen was cut perpendicular to the crystallographic axis.

quently, our statement[21,25] that the above bands in the spectra of fused quartz and of glass are not analogues, is fully corroborated by calculation.

A theoretical interpretation is similarly found for several other experimental facts, observed by the authors:[24,25] particularly, that the band with frequency near 1070 cm^{-1} in the spectrum of sodium metasilicate is depolarized or at least only partially polarized; that the bands with frequencies from approximately 525 to 600 cm^{-1} in the spectra of all types of glass are very intense and polarized, etc. Only in some details of little importance does a theoretical analysis refine and correct our conclusions in references 21 and 25.

In connection with the theoretical analysis of the spectra of silicate glass, we must dwell specially on the problem of the structure of the simplest type of glass—glass-like silica (fused quartz). The following problem is frequently raised in experimental investigations: what does the structure of glass-like silica approximate more closely, crystalline quartz or cristobalite? Since the Raman spectrum of cristobalite is still unknown, only one possibility remains, that of comparing the spectra of glass-like silica and crystalline quartz. As early as in 1928,[34] E. F. Gross and M. F. Romanova established the great similarity between the spectra of the two materials. Considerably later, in 1952, E. F. Gross and V. A. Kolesova confirmed these results and noted that the "broad bands in the spectrum of glass-like quartz are located in approximately the same positions as the sharp pronounced lines in the spectrum of crystalline quartz."[80] Other authors, citing analogous data, do not specially emphasize the similarity, leaving the readers to judge for themselves.

Thus it appears that one can conclude that there is a similarity in the structural lattices of glass-like silicon and of crystalline quartz. In other words, one can assume that the SiO_4 tetrahedra in glass-like silicon make with each other on the average an angle of 147°, which is characteristic of quartz.

However, one year later (1953) E. F. Gross and V. A. Kolesova stated that there is no similarity in the spectra and consequently in the structure, of crystalline and fused quartz. They stated that the latter more likely has the structure of cristobalite, but do not cite thereby any new spectroscopic data.[47] As arguments in favor of this assumption, Gross and Kolesova cite the results of an investigation on glass-like silica by roentgenoscopic methods and by the method of neutron diffraction, the results of
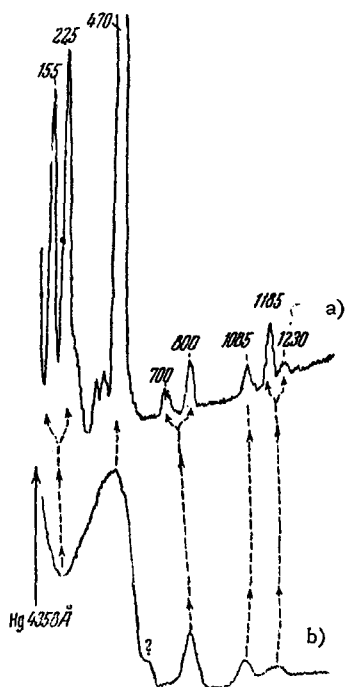
TABLE V. Comparison of data on frequencies in the spectra of
crystalline and fused quartz obtained by
various authors

Crystalline quartz (frequencies in cm⁻¹)			Fused quartz (frequencies in cm⁻¹)				
Gross and Romanova[34]	Kujumzelis[37]	Bobovich and Tulub	Gross and Romanova[34]	Kujumzelis[37]	Krishnan[82]	Harrand[49]	Bobovich and Tulub*
125	127	155 (s)			30—120	95	
207	209	225 (s)	215				
264	266		265				
	295				285		
320			325	230—450		275—500	
358	357	350 (w)	365		370		
405	398	415 (w)	445		430		
	410						
463	465	470 (vs)					
503			500	500	495	500	500 (vs)
526	530						
585	570—600						
633			625	607	635	595—612	595—600 (w)
694		700 (w)	665		660		
746	740		741				
800	803	800 (w)	790—830	780—840	775—805	795—826	800 (m)
944	860—950				810—845	860	
1021	1025				825—940	910	
	1063						
1075	1083	1085 (w)	1020—1070	1030—1090	1022—1098	1020—1100	1065 (w)
	1100						
1163	1162	1185 (w)					
1220	1235	1230 (w)	1180—1230	1160—1230	1140—1245	1150—1250	1200 (w)
	1400—1600						

*The frequencies measured photoelectrically at the maximum of the bands.
Literature data on the frequencies are found in reference 25.
Symbols: vs — very strong, s— strong, m — moderate, w — weak.

surface examinations, and also the fact that cristobalite crystals are invariably precipitated during its devitrification.

In connection with the latter fact, we note the following. The very fact that one type of crystal or another is precipitated is not convincing proof of a corresponding structure of the original, non-crystallized body. To judge the structure of glass reliably, it is necessary to follow its "thermal life" step by step, as is done, for example, in the papers of V. A. Florinskaya and her associates.[50] At this point, E. F. Gross is again in contradiction with his own discussion of the glassy state, where he stated: "In fact, it is impossible to consider crystallized glass, in which crystals of various silicate compounds are precipitated, as a certain analogue of the structure of the true homogeneous glass. It would not occur to anyone to consider a liquid in which crystals are precipitated as a system similar in structure to the true liquid."[81]

It appears to us that even raising the question of comparison of the vibrational spectra of fused quartz, crystalline quartz, and cristobalites, is rather meaningless. In fact, at ordinary temperatures fused quartz can contain only the α-modification of crystalline quartz or cristobalite. Their

similarity is so great that one can hardly expect great spectroscopic differences. On the contrary, the β-modifications are substantially different. However, they are stable only at high temperatures.

Nevertheless we thought it advisable to compare the Raman spectra of glass-like silica and of crystalline quartz, obtained under identical conditions. These spectra are shown in Fig. 25. To evaluate their reliability, we selected data on both spectra from the best investigations.

A careful study of the data given in Table V, taken from various sources, permits the conclusion of a sufficiently good agreement as regards the principal lines and bands. On the other hand, we see also a close agreement between the spectra of glass-like silica and crystalline quartz. The existence of several weak lines, the very reliability of which can be doubted, in the spectrum of the crystalline quartz can hardly serve as an argument against this conclusion. Consequently, the experimental data on Raman spectra of glass-like silica and crystalline quartz are compatible with the assumption that their structural lattices are analogous.

The results of the theoretical calculations con-

firm well the conclusions of the experimental research. According to calculations, the spectrum of glass-like silicon is characterized by two sufficiently intense bands, one very intense and polarized at the low-frequency boundary of the investigated region, and another weaker one, depolarized in the central region. The remaining bands should be weak and depolarized. All this is, indeed, observed experimentally. The small discrepancy between the calculated and observed values of the frequencies in the range from 1180 to 1100 and from 1150 to 1250 cm^{-1} is explained by the fact that reference 25, on which the calculation is based, has incorrect values of the maximum frequencies of these bands. The use of exact experimental values (see Table V) leads to good agreement in the results. Were the glass-like silica closer in structure to cristobalite than according to the calculations, its spectrum would contain only one intense band.

It must be noted that in one substantial detail the experimental and theoretical data are still in disagreement. As was shown by Harrand[49] and by the authors,[25] a polarized band is observed in the spectrum of glass-like silica in the region around 600 cm^{-1}. The possibility of an experimental error must be excluded. Yet, according to calculations, this region should contain a depolarized band. One can therefore assume that the glass-like silica contains additional structural formations, although, judging from the intensities of the bands, the quartz-like formations predominate.

In connection with the discussion of the problem of the structure of glass-like silica, it is appropriate to cite certain results obtained by the method of infrared spectra. The advantage of this method, incidentally, consists of the relative ease with which minute crystals and powdered substances can be investigated. It is in exactly this form that cristobalite and tridymite can be prepared. That is why it has been possible recently to obtain and compare the spectra of all modifications of quartz.

Infrared spectra are usually studied in absorption or reflection. However, only the absorption spectra have a simple physical meaning. Generally speaking, the absorption spectra can be obtained from the reflection spectra through computation. However, the computational method, owing to certain arbitrariness in the initial assumptions, may lead to systematic errors in the results. This is why data on absorption spectra and conclusions on the structure of glass-like silica, made by several authors using the computational scheme[76] are always under doubt.

It is much more advisable to compare only transmission spectra or only reflection spectra.

This is indeed the procedure used by V. A. Florinskaya and her associates.[72,150,83] According to their data, vitreous silicon is closer in its structure to crystalline quartz than to tridymite or cristobalite. This supports the conclusions based on an investigation of Raman spectra of certain of these bodies, and also the results of the theoretical calculations.

Conclusions. One can state that the theoretical calculations confirm the point of view that alkali-silicate glass is structurally inhomogeneous, as expressed in references 21, 24, and 25 on the basis of experimental investigation of their Raman spectra. The theoretical results are compatible with the assumption of a layered structure of glass with a composition of bisilicate. This is equivalent to saying that a chemical formula can be given for these types of glass. In accordance with the experimental data, calculations show that the glass-like silica is closer in structure to crystalline quartz than to cristobalite. From the very character of the calculation it follows that it is possible to consider various structural formations in glass as crystallites in the ordinary sense of the word.

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