

Radiation-induced states in crystals with ionic-covalent bonds

E. V. Kolontsova

*M. V. Lomonosov State University (Moscow)*Usp. Fiz. Nauk **151**, 149–172 (January 1987)

Based on a review of data in the literature and on the results of a systematic investigation of the effect of various kinds of radiation on a number of crystals with ionic-covalent bonds (ICB crystals), the author describes mechanisms and regularities associated with the creation of radiation-induced structural states. A classification of these states is given, along with their characteristics and models of their behavior. The author proposes a criterion, tested on specially selected compounds, for high-temperature structural instability leading to the realization of a structural state, which in terms of the symmetry and parameters of the unit cell is close to the high-temperature modification of the unirradiated crystal. As a basis for choosing this special class of compounds thermodynamic parameters are adopted which determine the character of their thermal phase transitions. It is shown that, apart from amorphization and decomposition of the original compound, this is the only possible overall change in the structure of ICB crystals which extends throughout their entire volume. The author concludes that for the majority of ICB crystals in which such changes in crystal structure are observed, a decisive role is played by isolated point defects caused by radiation. She also investigates the influence of impurities, growth conditions and conditions of irradiation on the radiation hardness of a structure. In conclusion, she points out factors which determine the structural states of an irradiated ICB crystal, and analyzes the causes of discrepancies in the experimental data of various authors regarding the effect of radiation on the structure of the same material.

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1. INTRODUCTION

In an era of large-scale development of nuclear energy, the study of changes in the physical properties of irradiated crystalline bodies, along with the question of how radiation acts on a crystal structure, have become very pressing problems in solid-state physics and in material science of irradiated substances. Fundamental aspects of these problems which are of great practical significance are those which relate to the creation of materials with improved and novel properties, and to the control of radiation hardness of solids.

It is obvious that the solution to these problems depends on how well we understand the structural states which are created by the action of various kinds of radiation on crystals with a given initial structure and interatomic bonds, and how the creation of these new states depends on impurities, growth conditions and conditions of irradiation. All these factors determine the character of the resulting defects, i.e., their forms, sizes, orientations and locations throughout the volume of an irradiated crystal; in addition, they can play a fundamental role in determining the susceptibility of a crystal structure to a partial or total rearrangement at a certain level of irradiation.

In this article an attempt will be made to describe basic regularities in the creation of structural states in crystals with ionic-covalent interatomic bonds under the action of irradiation with neutrons (n), electrons (e), and γ - and x-ray quanta, based on the aggregate of published data obtained by a combination of direct methods of investigation which allow defect and crystal structures to be studied practically at the atomic level without introducing additional changes in the course of the investigation.

In generalizing the data in the literature, the analysis presented in this paper takes into account factors such as differences in the dominant mechanisms by which primary defects are formed when different forms of radiation are used, the irradiation conditions, and the presence of growth-induced defects and impurities; these factors determine the interaction of radiation-induced defects with one another, with defects of pre-irradiation origin and with the surrounding ions (atoms) of the crystal under study.

In order to clarify the mechanism of formation of complex secondary defects which appear as a result of this interaction along with the rearrangement of the crystal structure caused by displacement of atoms, data have been included from investigations of the effect of heating on irradiated and unirradiated crystals; this data is examined in conjunction with the study of the dose dependence of structural states. In taking stock of this data, there is a decided preference for experimental investigations carried out on single crystals, and this is very important if the results obtained are to be unambiguously interpreted. In addition, studies were made not only of the action of various forms of radiation on one specific material, but also of the influence of one specific kind of radiation on several crystals, with different atomic bonds and structural features; these considerations have a fundamental value in establishing general regularities which are observed in the formation of radiation-induced structural states.

The appearance in a crystal of deviations from the regular crystal structure under the action of radiation will in general result in changes in its defect and crystallographic structures. The mechanisms of formation of primary radiation-induced defects, and the fundamental characteristics of the secondary defects which appear as a result of interaction among these primary defects, as well as the changes in dislocation structure, have been most fully studied for model alkali-halide crystals (AHCs) with NaCl structure. Such crystals are convenient systems in which to study regularities in the way a defect structure changes at each stage of irradiation, both from a methodological standpoint and because their crystallographic systems do not change under the action of radiation despite the presence of atoms in the neighborhood of a defect which are displaced relative to their original stable equilibrium positions.

The crystal LiF occupies a special place among the AHCs with NaCl structure. The concentration of point defects in n-irradiated LiF can attain very large values, which is an essential condition for the study of interactions between defects. These high concentrations are due to the fact that, in addition to the direct effect of the neutrons, atoms of helium and tritium, which appear as a result of the reaction $\text{Li}^6(n, \alpha)$, act on the crystal structure at the same time. The amount of the isotope Li^6 in LiF is rather appreciable,

$\sim 7.5\%$, while the energies needed to release α particles and tritium equal 2.1 and 2.7 MeV respectively.

It is appropriate to describe the observed regularities in radiation-induced changes in the crystal structures of compounds of interest in terms of their structural and thermodynamic characteristics, i.e., within the scheme of well-known descriptions of the mechanisms and criteria for radiation-induced structural instability. In addition, it is expedient to take into account the interatomic bond energy, since the processes which result in decomposition of the original compound into its constitutive elements, and which compete with the crystal rearrangement, can completely mask the process of structural change. On the other hand, crystals with relatively weak interatomic bonds are particularly interesting, because we can estimate the role of point defects in the reconstruction process by investigating the influence of γ - and x-ray irradiation on their structure. With this in mind, in order to illustrate the basic regularities which characterize the creation of structural states in the course of radiation-induced crystal rearrangement, crystals were chosen in which these changes in crystal structure have been most fully studied, i.e., the neutron-irradiated α - SiO_2 , BaTiO_3 and in γ -irradiated crystals of CsNO_3 and NaNO_2 .¹⁾ It is convenient to trace the influence of impurities, growth conditions and irradiation on the kinetics of the reconstruction process using these particular compounds.

2. THE BASIC TYPES OF RADIATION-INDUCED STRUCTURAL STATES: MECHANISMS AND REGULARITIES IN THEIR FORMATION

Based on generalizations derived from the results of investigating n-, e-, γ - and x-irradiated crystals, we can conclude that, with regard to the nature of structural changes observed under the action of radiation, there are three types of primary structural states (in addition to amorphization) observed in those crystals with ionic-covalent bonds investigated up to the present time.

The best-known radiation-induced structural states—type I in our terminology—are characterized by a change in the defect structure caused by interaction of the primary radiation-induced defects among themselves and with defects of pre-irradiation origin. Various sorts of secondary defects are created as a result of this interaction; the concentration of these defects changes as well as their locations throughout the volume of the irradiated crystal. In some compounds the original crystal structure remains unchanged up to complete amorphization or mechanical destruction of the crystals, which are observed under specific conditions of irradiation. Type II structural states can be regarded as configurational changes in the local environment of atoms, or within localized regions of the crystals, which do not lead to an obvious change in the crystallographic systems which underlie the structure of these crystals. For type III structural states, the change in crystal structure occurs characteristically throughout the entire volume of the irradiated crystal, and is accompanied by a transition at a specific level of irradiation to a structure which corresponds in symmetry to that of a high-temperature modification of the unirradiated crystal. Provisionally these changes will be referred to as “radiation-induced phase transitions.”

In all three of the aforementioned types of structural states, the formation of the new state is accompanied, as a rule, by amorphization within a localized region of the crystal in the initial stages of irradiation. As the dose increases, we observe an increase in the volume of the amorphized region until a transition occurs to the amorphous state throughout the entire irradiated crystal. In some compounds, amorphization takes place within the entire crystal volume and there is no clear sign of crystal structure modification.

We should stipulate that within the postulated scheme of structural states there is no separate treatment of radiation-induced decomposition of the original compound, an effect which is observed in the majority of investigated crystals and which is initiated by a certain level of radiation dosage. This process, which competes with the formation of the three types of structural states enumerated above, is accompanied by the creation of new compounds or separation of the compound under irradiation into its original elements.

2.1. Defect structure of irradiated crystals

As mentioned above, the type I structural states which have been most thoroughly investigated are those which occur in AHCs with NaCl structure. In this article we will not pause to discuss any results which pertain to formation of primary defects, since there are detailed reviews and complete monographs²⁴⁻²⁶ on this question; instead, we will investigate regularities in the formation of secondary defects, with the help of methods such as investigation of the dependence of the diffuse x-ray scattering intensity J_{diff} on distance q from a point of the reciprocal lattice, and studying the distribution of this scattering over a wide region of reciprocal space; 2) in addition, data from electron-microscopy analysis and selective etching used in combination allow us to obtain detailed secondary-defect parameters at the atomic level.

By comparing data on the behavior of radiation-induced defects when irradiated crystals are annealed with data derived by other methods, we are led to conclude that point defects generated by n-, e-, γ - and x-radiation form stable clusters of roughly equiaxial form along with dislocation loops at some specific dose level. The sizes and concentration ratio of these defects depend on the type and conditions of irradiation.

For γ - and x-irradiation, the primary defects are dislocation loops.²⁷ In e-irradiated crystals, a tendency to form such loops is observed for lower beam fluxes; as the beam current increases, the tendency is to form stable clusters of point defects.²⁸ For n-irradiation the concentration ratio between these types of defects depends primarily on dose and temperature. For low doses, dislocation loops predominate,^{27,29,30} while the average sizes of the defects lie in the range 40–100 Å.^{27,31} As the dose and irradiation temperature T_{irr} increase, a redistribution in sizes is observed along with a shift in the distribution maximum to the region of larger values.

The interrelation between the creation of point defects and the growth process for secondary isotropic defects in irradiated AHCs, taking into account T_{irr} and the magnitude of the dose, is investigated in Ref. 32. In this reference a theoretical model of the growth process is also given which

takes into account both the primary defect-creation events and the basic characteristics of radiation-stimulated aggregation.

We do not observe creation of anisotropic damage in e-irradiated single-crystal AHCs over the entire investigated dose interval ($\sim 10^{15}$ – 10^{19} /cm²) if the mean free path of the bombarding electrons is longer than the thickness of the irradiated crystals. In the opposite case, as charge is accumulated, there appear rod-shaped macro-defects parallel to the $\langle 100 \rangle$ directions, whose concentration increases with irradiation dose.²⁸

Stable clusters of anisotropic shape are distributed in an oriented fashion relative to the lattice of the original crystal; with regard to the multiplicity of secondary defects, the richest "landscape" forms in n-irradiated crystals of LiF, beginning with a dose of $\sim 10^{17}$ n/cm².^{23,24,31} From the ensemble of available data we can conclude that as the dose is changed from $\sim 10^{17}$ to 10^{19} n/cm² and the irradiation temperature is changed from $\sim 70^\circ$ to 250° C, certain types of oriented defects are created which are stable not only at room temperature but also at somewhat higher temperatures. Prominent among these are vacancy clusters of sheetlike form parallel to the $\{100\}$ planes, and various kinds of two-dimensional damage in the $\{111\}$ planes (Fig. 1). In addition, for irradiated crystals at dose 10^{18} n/cm², the x-ray method reveals that metallic lithium precipitates out in three modifications: amorphous Li and two crystalline varieties with FCC and BCC lattices. The size of the Li inclusions is determined by the structure of the precipitated lithium and the irradiation conditions, while the orientational linkage with the original lattice is determined only by the structure of the precipitates.³⁴

Differences in irradiation temperature have an important influence on the character and stability of the two-dimensional $\{111\}$ damage (see Fig. 1), on the size distribu-

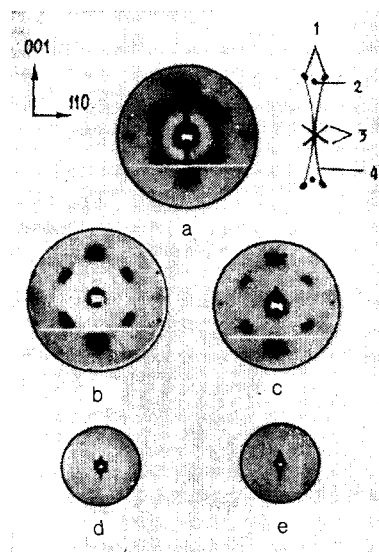


FIG. 1. Oriented defects in single crystals of LiF irradiated by neutrons. $F \sim 5 \times 10^{18}$ n/cm²; $E > 0.5$ MeV. a, b, d— $T_{\text{irr}} < 100^\circ$ C, c, e— $T_{\text{irr}} > 150^\circ$ C. Monochromatic K_α Mo-radiation; a, b, d— $\theta = 1.5$ – 25° ; c, e— $\theta = 4$ – 3° . a—before annealing. b, d— $T_{\text{ann}} = 500^\circ$ C. c, e— $T_{\text{ann}} = 400^\circ$ C. 1—scattering of X-rays by defects of lamellar form, located in the $\{100\}$ plane; 2–3—the same for $\{111\}$; 4—scattering by rod-shaped defects oriented along $\langle 100 \rangle$.

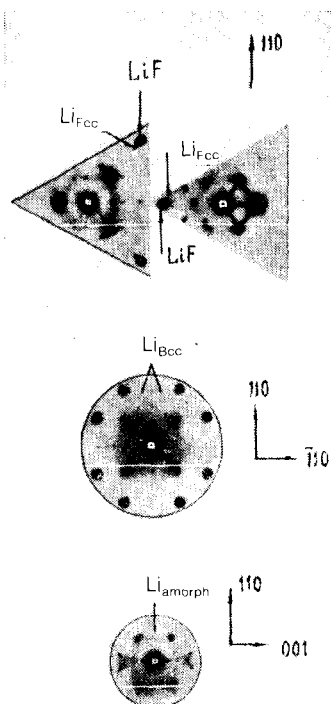


FIG. 2. Three modifications of lithium in single crystal LiF irradiated by neutrons. $F \sim 5 \times 10^{18}$ n/cm²; $E \geq 0.5$ MeV; $T_{irr} \sim 70^\circ\text{C}$. Monochromatic K_{α} Mo-radiation.

tion of vacancy clusters of both equiaxial and lamellar forms parallel to the (100) planes, and on the size and concentration ratios of the various modifications of precipitated lithium. The sizes of the two-dimensional (100) damage and thermally-stable (111) damage also depend in various ways on T_{irr} and the temperature of subsequent annealing. Under good heat-transfer conditions ($T_{irr} \sim 70^\circ\text{C}$) they are all of the same size and are roughly one atomic spacing ($\sim 4 \text{ \AA}$) in thickness, and no more than about twenty atomic spacings in size along the two other dimensions. As the temperature increases, only an insignificant increase is observed in the longitudinal sizes of the lamellar (111) structures, while the vacancy interlayers parallel to the (100) planes coagulate, forming pores whose average size is 10–20 μm .

The FCC modification of lithium is less stable relative to temperature, while the amorphous lithium is least stable; the temperature stability boundary of the most stable modification—the BCC lithium Li_{BCC} —is determined by T_{irr} and coincides everywhere with the stability boundary of the two-dimensional (111) damage.³⁵ This points to a connection between the size dependence of the Li_{BCC} precipitates on T_{irr} and the coherence of the linkage between the LiF and Li_{BCC} lattices $(111)_{\text{LiF}} \parallel (110)_{\text{Li}_{\text{BCC}}}$.

At this point, it behooves us to turn our attention to the following fact; the shape of the clusters, the orientation of the anisotropic structural defects relative to the lattice of the original crystal and the positions of the clusters throughout the volume of the irradiated crystal all depend on dose and not on the type of radiation. The electron-microscope method reveals two-dimensional damage oriented along (100) in e-irradiated thin films of NaCl and KCl.³⁶ It is true that

researchers have also observed the formation of two-dimensional damage oriented along (100) at certain levels of x-irradiation which is different in character from the stable vacancy clusters which form in n-irradiated single crystals of LiF; however, this damage is observed in NaCl, not in LiF crystals.³⁷ Analysis of x-ray diffraction effects and data from the selective-etch method shows that the appearance of this damage is due to the creation of oriented dislocation loops.^{27,28,4)}

From the character of the distribution and dependence of the diffuse scattering intensity on dose, and also from calculations,³⁸ it follows that for small concentrations the damage clusters are located in a disordered fashion throughout the volume of the irradiated crystal, whereas at a specific level of n-, e- or x-irradiation the two-dimensional (100) damage regions arrange themselves sequentially along the (100) direction.²⁷

A factor which is no less important, especially with regard to the appearance of the above-mentioned defect structure under irradiation, is the manner in which the details of formation of secondary defects, along with their sizes and concentration, depend on the mechanism by which the primary radiation-induced defects are formed, as well as the rate at which diffusion processes transfer these defects; this dependence was described in Ref. 27. In addition to the above-mentioned differences in dose dependence which characterize the formation of oriented defects in LiF and NaCl crystals under n- and x-irradiation, it is sufficient to cite the value of the magnitude of the intensity increment ΔJ_{diff} at the diffusive scattering maximum, which is uniquely related to the concentration of point defects and their clusters. For n- and e-irradiation, J_{diff} increases by 500–700% for LiF, starting at a dose of $\sim 10^{17} \text{ cm}^{-2}$, while for NaCl and KCl it increases by no more than 20% even for doses $> 10^{18} \text{ n/cm}^2$,²⁸ although the compliance to radiation-induced damage should be higher in NaCl and KCl crystals, since in the series LiF, NaCl and KCl, LiF possesses the largest binding energy. This difference cannot be explained by invoking the special effect of neutron irradiation, i.e., the reaction $\text{Li}^6(n, \alpha)$ in LiF, because analogous behavior is also observed for e-irradiation.

The difference in character and importance of radiation-induced effects in LiF, NaCl and KCl crystals at various stages of n-, e- γ - and x-irradiation can be understood if we take into account the different rates at which diffusion processes occur against the background of differences in the concentration and in the character of the distribution of primary radiation-induced defects, depending on whether they were created with the help of impact or non-impact mechanisms.

At normal irradiation temperatures ($T_{irr} \geq 40^\circ\text{C}$), processes involving both creation and annihilation of point defects take place at the same time, along with those which involve formation and coagulation of clusters and which lead to the "healing" of the latter. From the results and data obtained from measurement of the self-diffusion coefficients,^{39,40} it follows that processes based on the migration mobility of defects and atoms occur with significantly more activity in NaCl and KCl than in LiF. This conclusion is illustrated with particular clarity by the regularities which have been identified in the way that dislocation structures

change in irradiated crystals.⁴¹ The rearrangement of these structures begins, just as in the case of heating, by creeping of individual dislocations. Again just as with heating, the general tendency is towards a decrease in the density of isolated dislocations as the dose increases and the creation of dislocation "walls," which as a rule are parallel to the (100) planes. Comparison of this data for γ -irradiated and annealed unirradiated crystals of LiF and NaCl shows that each interval of investigated dose can be put into direct correspondence with a specific temperature interval; the rate of dislocation creep depends not only on the dose but also on the material. For the same doses of irradiation this rate is smaller for LiF crystals.⁴¹

In this way, processes of radiation-induced annealing of point defects and coagulation of clusters of these defects in irradiated crystals of NaCl and KCl can successfully compete with the formation of stable nucleation centers and the creation of more of the small-sized clusters, since the processes connected with radiation-stimulated diffusion occur in these crystals more actively than in crystals of LiF.⁵¹ In addition, if the basic mechanisms by which radiation-induced defects are formed were connected with the excitation of the electronic subsystem, and consequently with the appearance of point defects distributed more or less uniformly throughout the volume, than the interaction of the stress fields of point defects could not play a decisive role in the creation of secondary defects. In real crystals, which contain as a rule no less than 10^4 – 10^5 dislocations/cm², it is more probable that the point defects interact with dislocations, especially at low to medium radiation doses; as a result of this interaction, conditions are created under which dislocation loops can form with the help of dislocation creep. This scenario is confirmed experimentally on the example of γ - and x-irradiation of NaCl crystals.

Thus, despite differences related to diffractive effects for n-, e-, γ - and x-irradiated crystals, radiation-induced changes in the defect structure of AHCs as revealed by various methods are always subject to certain regularities. Analysis of these effects indicates that they only give rise to differences in the stress fields caused by secondary defects—i.e., various kinds of complexes and clusters of point defects—and differences in their concentrations and average sizes. Important factors in determining the character of these secondary defects—their form, size and orientation relative to the original crystal lattice for $T_{\text{irr}} \geq 40^\circ\text{C}$ —are the concentration of point defects injected by irradiation, their distribution throughout the volume and their mobility, whose value in general depends on the type of irradiation used as well as its energy spectrum, dose and irradiation temperature, and also on the shelf-diffusion coefficient and on defects of pre-irradiation origin.

Analysis of well-known data on the variation of defect structure in other irradiated crystals with ionic-covalent interatomic bonds allows us to conclude that the regularities in formation of secondary defects which have been identified in NaCl-structure alkali halide crystals are in fact general in character.

2.2 Configurational changes in structure

All the results described above refer to the appearance in irradiated crystals of some kind of defects located either

randomly throughout the volume of the crystal or in the form of sequences along definite crystallographic directions (clusters of point defects and dislocation loops). The average stable equilibrium positions of atoms in AHCs for $T_{\text{irr}} \geq 40^\circ\text{C}$ do not change, in some cases up to irradiation levels which give rise to mechanical destruction of single crystals.

Marked (i.e., detectable) changes in crystal structure of nonmetals under the action of radiation are observed only in those compounds whose structure does not possess sufficient thermal stability, and in which phase transitions occur upon heating the unirradiated crystals. In all such compounds, the radiation-induced rearrangement of the crystal structure which occurs is a high-temperature type of rearrangement, brought about by the formation of structural states close to the high-temperature modification of the unirradiated crystal.

We succeeded in showing that under certain conditions of irradiation by neutrons, configurational changes in structure appear in single crystals of LiNbO₃ (at doses $\sim 3.6 \times 10^{20}$ n/cm², $E \approx 0.5$ MeV, $T_{\text{irr}} \approx 150^\circ$) and LiF (in the dose interval 10^{17} – 10^{18} n/cm², $E \approx 0.5$ MeV, $T_{\text{irr}} = 15^\circ$ and 100°K), which are not associated with changes in the type of crystal lattice of the sort which take place during a radiation-induced high-temperature type of crystal structure rearrangement. We are led to this conclusion after analyzing data obtained by the diffuse scattering method.^{24,42} The essential changes in the intensity distribution of diffuse scattering observed over a broad region of reciprocal space in irradiated crystals of LiNbO₃ and LiF^{43,44} do not correspond either to a clear crystal rearrangement or to the theoretical descriptions of scattering from some well-known defect structures distributed randomly throughout the irradiated crystal volume.

Taking into account the theory of diffuse scattering, the changes observed in Ref. 43 with regard to the ratios of diffuse-scattering maxima, the redistribution of J_{diff} in the neighborhood of certain points and individual portions of planes of the reciprocal lattice, and also the appearance of additional scattering in a wide region of reciprocal space for LiNbO₃ (Fig. 3), all clearly point to changes in the positions of atoms, if only in localized regions of the irradiated crystal. After analyzing the results of measurements of unit-cell parameters under irradiation, and of observations of the variations in single-crystal LiNbO₃ by the diffuse-scattering method under irradiation, heating and deviation from stoichiometry,^{43,45} and also taking into account the data on changes in parameters and investigating the nature of defects in crystals of non-stoichiometric composition,^{46,47} we are led to conclude that the basic changes in the structure of irradiated crystals are connected with disruption of stoichiometry and the ordered positioning of Nb⁵⁺ ions next to vacant Li positions along certain crystallographic directions ($\langle \bar{2}21 \rangle$).

It should be noted that, although for all the above-mentioned perturbations the atomic displacements are connected with changes in the same crystallographic element, analysis of the distribution of J_{diff} shows that important differences are observed in the details of the change in atomic positions for irradiation, heating and deviation from stoichiometry.^{27,45} Differences in the structural states formed in irradiated and heated crystals are apparent not only from the

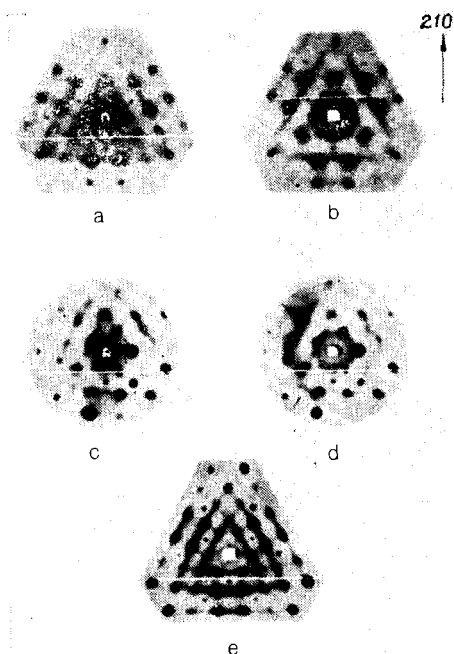


FIG. 3. Change in the intensity distribution of diffuse scattering of x-rays by single crystals of LiNbO_3 upon heating and upon irradiation. $F \sim 3.6 \times 10^{20} \text{ n/cm}^2$; $E > 0.5 \text{ MeV}$; $T_{\text{irr}} \sim 150^\circ \text{C}$. Monochromatic K_α Mo-radiation. a, b, e—the $[001]$ direction parallel to the beam; c, d—this direction inclined by 8° .

results of diffuse-scattering measurements. From measurements of unit-cell parameters it follows that the change in these parameters under irradiation does not correspond to well-known data on the temperature dependence of these quantities.^{43,48,49}

In the investigated intervals of dose (up to $\sim 4 \times 10^{20} \text{ n/cm}^2$), temperature (up to 800°C) and departure from stoichiometry (1 to 0.89 lithium deficiency) the structural type did not change.

The character of diffuse scattering, which was investigated over a wide region of reciprocal space, was the same for irradiation of LiF single crystals at $T_{\text{irr}} = 15^\circ$ and 100°K , and differed fundamentally from the way the scattering picture was observed to change at $T_{\text{irr}} \sim 70^\circ \text{C}$ (Fig. 4). Analysis of the experimental data shows that scattering in LiF single crystals irradiated at low temperature does not correspond either to the effects of shape or to the usual development of two-dimensional and one-dimensional diffraction patterns of the sort observed after irradiation under normal conditions. The character of the diffraction effects does not permit us to classify them as satellites either; nor can these changes be explained by postulating that well-known defects are distributed randomly throughout the volume of the irradiated crystal.

Comparison of overall regularities in the variation of diffuse scattering in n-irradiated crystals of LiNbO_3 and LiF ($T_{\text{irr}} = 15^\circ$ and 100°K) taking into account the character of the intensity distribution, the regularities in the way additional diffraction effects differed near sites of different type, and also data obtained by comparing the temperature dependence of the intensity of additional scattering⁴²⁻⁴⁴ allows us to postulate an ordered positioning of point defects which is

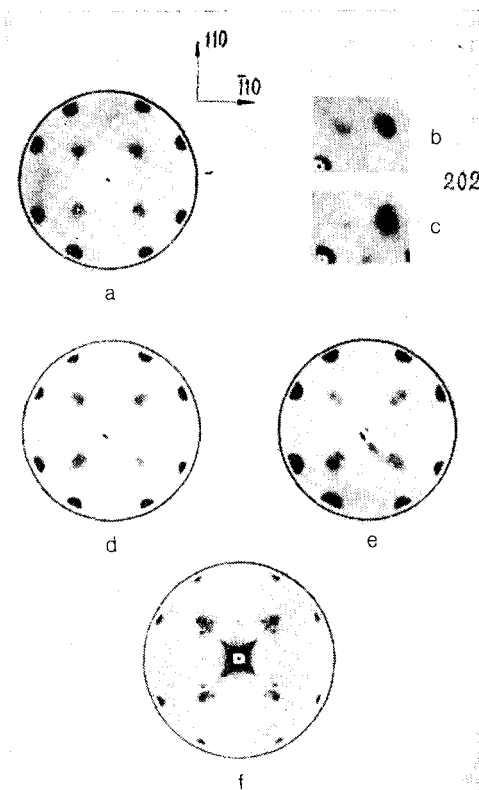


FIG. 4. Structural states formed in LiF single-crystal irradiated at various temperatures. Monochromatic K_α Mo-radiation. a, b—unirradiated. c, d, e— $T_{\text{irr}} \sim 100^\circ \text{K}$. f— $T_{\text{irr}} \sim 70^\circ \text{C}$. a, b, c, d, f—temperature of the x-ray film is $\sim 20^\circ \text{C}$. e— $\sim 100^\circ \text{C}$.

specific to each type of lattice, of a kind closer to the type II structural states. Because of this, we observe configurational rearrangement in the immediate neighborhood of atoms associated with changes in the potential energy of the interatomic interaction and correspondingly with changes in the vibrational spectrum of localized regions of the crystal. From the diffuse-scattering results before and after annealing we can conclude that vacancies⁴⁴ are the primary defects of this sort in LiF ; the shifts in atomic positions caused by them have a static character and basically are determined by the strength of the interatomic interaction.

It is possible that the changes exhibited by $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4$ (TGS) under irradiation with small doses of x-rays,^{50,51} which are caused by the peculiar ordering in the positions of hydrogen ions, can be related to configurational structural changes. As also in LiNbO_3 , these changes differ from those changes observed upon heating TGS.

2.3. High-temperature types of structural rearrangement in crystals

The most carefully studied type III structural states occur in single-crystal quartz.^{7-10,27,43,45} Investigations of the intensity distribution of diffuse scattering, conducted over a wide region of reciprocal space, in n-irradiated and unirradiated crystals in the interval $20-750^\circ \text{C}$ have shown that the dose dependence of the radiation-induced states is qualitatively analogous to the temperature dependence in the pre-

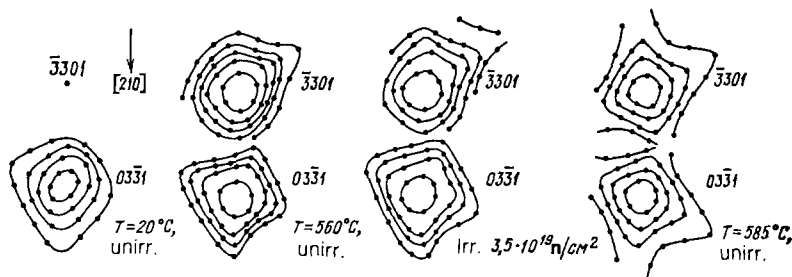


FIG. 5. Change in the intensity distribution of diffuse scattering of K_{α} Mo x-rays in the vicinity of reciprocal lattice sites for native quartz in the case of irradiation by neutrons and near the α - β transition.

phase transition regime.^{9,10,27,43} However, an analysis of the temperature dependence of diffuse scattering by irradiated and unirradiated crystals proves convincingly that the atomic displacements responsible for the rearrangement of the structure of irradiated crystals are static in character,^{9,10,43} whereas from inelastic neutron scattering data one can conclude with no less assurance that the α - β transition in unirradiated quartz crystals is mediated by dynamic shifts of the atoms.⁵²

A study of the influence of annealing shows that structural states created under the action of radiation are stable over a wide temperature range (including room temperature); this stability increases with the radiation dose.⁸ Based on this, and also on the agreement between the observed variation in diffuse scattering and structural parameters due to irradiation and that due to the α - β transition, we confirm that these states are in fact novel structural states, intermediate between the low- and high-temperature modifications (Figs. 5, 6; Tables I, II). This conclusion is of considerable interest; from it follows the fact that irradiation allows us to realize structural states which are stable at room temperature and which are close to any state which arises in unirradiated crystals during the pre-phase transition stage, since the magnitudes of the atomic displacements from their equilibrium positions are determined by the dose (see Table II).

From a comparison of the anisotropies in the changes in unit-cell parameters (see Table I), we can conclude that the radiation-induced rearrangement of the crystal structure in quartz is not related to the creation of nuclei of the high-temperature modification, nor to growth of the volume of these regions under irradiation. As is clear from the data presented, for doses $\sim 4 \times 10^{19}$ n/cm² the lattice parameter a increases by 1.65%, c by 0.56%, i.e., the increase in a exceeds the increment of c by roughly a factor of 3 in irradiated crystals; by contrast, in the phase transition $\Delta a/a$ exceeds $\Delta c/c$ by no more than a factor of 1.5.⁵⁵

Analysis of the results presented in Refs. 8–10, 27 and 43 on the study of diffuse scattering over a wide range of reciprocal space for irradiated and heated unirradiated crystals allows us to conclude that the simple models of planar and linear disorder postulated to describe the α - β transition,⁵⁶ and the change in structure under irradiation,⁵⁷ do not correspond to the observed changes in quartz under heating and irradiation (see Fig. 6).

Investigation of $\Delta J_{\text{diff}} = f(q)$ for those stages of irradiation at which clear structural rearrangement is observed shows that the primary defects are isolated point defects ($\Delta J_{\text{diff}} \sim 1/q^2$).²⁷ These data, along with results obtained by the diffuse-scattering and diffractometer methods,^{8,10,43,45} allow us to confirm that the radiation-induced structural rearrangement in quartz is caused by directional correlation of the atomic displacements caused by point defects. This conclusion, which is of considerable importance in determining the mechanism which mediates changes in crystal structure of irradiated crystals, can in all probability be applied also to neutron-irradiated crystals of BaTiO₃; it is further confirmed by data on the change in diffuse scattering of x-rays observed upon heating single crystals,⁵⁸ by the analysis of dose dependence of the unit-cell parameters in neutron-irradiated polycrystalline samples, by comparison of the variation in intensity of x-ray and neutron scattering, by data on the infrared absorption and by results of studies of dielectric properties under irradiation.^{16,59}

Other compounds of this type, such as PbZrO₃ and KNbO₃, have been less studied; in these compounds, radiation-induced rearrangements of high-temperature type have been observed under the action of neutrons.^{13–15,18} However, in these crystals too the rearrangement apparently takes place because of directional displacements caused by point defects of radiative origin (according to data on diffuse scattering by heated single crystals⁶⁰ and dose dependence of unit-cell parameters¹³). Finally, from the variations in

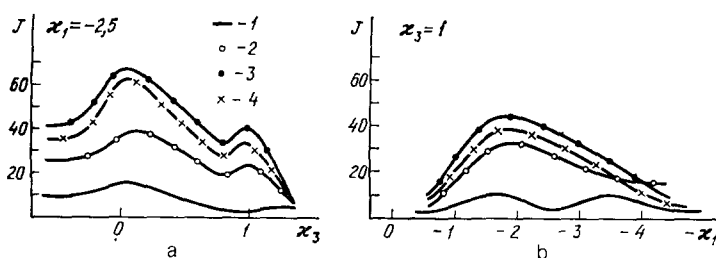


FIG. 6. Intensity distribution of diffuse scattering of K_{α} Mo x-rays between reciprocal lattice sites in irradiated and unirradiated native quartz. \mathcal{H} -coordinates in reciprocal space. 1—unirradiated, $T = 20^\circ\text{C}$; 2—unirradiated $T = 500^\circ\text{C}$; 3—unirradiated, $T = 560^\circ\text{C}$; 4—irradiated, $\sim 3.5 \times 10^{19}$ n/cm² ($E \geq 0.5$ MeV; $T_{\text{irr}} \sim 100^\circ\text{C}$).

TABLE I. Unit-cell parameters of α -quartz irradiated by neutrons.

Dose, n/cm ²	<i>a</i> , Å	<i>c</i> , Å	ρ , g/cm ³
Unirradiated α -SiO ₂ ⁵³	4,912 (2)	5,398 (1)	2,63
3·10 ¹⁹	4,959 (2)	5,419 (1)	2,59
3,5·10 ¹⁹	4,965 (2)	5,424 (2)	2,58
4·10 ¹⁹	4,993 (3)	5,428 (3)	2,55
β -SiO ₂ ⁵⁴	4,997 (1)	5,460 (1)	2,53

structure of the crystal CsNO₃ under γ - and x-irradiation,²¹ and from those of the crystal NaNO₃ under γ -irradiation²⁰ which were discovered last year, it follows directly that for a number of compounds the parameter which determines radiation-induced structural instability of high-temperature type is the concentration of isolated radiation-induced point defects. The data described below concerning the influence on the kinetics and structural rearrangement of impurities, radiation-induced annealing, growth-induced defects and defects originating from deformation definitely confirm this conclusion.

3. A CRITERION FOR STRUCTURAL INSTABILITY OF IRRADIATED CRYSTALS

The development of a description of the rearrangement mechanism is intimately related to the question of criteria for radiation-induced structural instability. This question, which still has not been totally resolved, has also a value in its own right, since in order to produce radiation-influenced changes in the properties of a crystal one must know the conditions under which the crystal structure can be changed by the action of radiation, and in particular the necessary and sufficient conditions for a complete high-temperature structural rearrangement—up until now the only type, besides amorphization and decomposition of the crystal, of radiation-induced change in the crystal structure which takes place throughout the entire volume of irradiated material.

Based on a critical analysis of those papers from which one can extract information (even if it is only indirect) related to radiation-induced structural instability, one may draw the conclusion that the assumptions stated earlier concerning the constraints imposed on the structure and character of a phase transition in a crystalline body cannot be considered as sufficient conditions to guarantee a rearrangement.

It is obvious that for the radiation-induced high-temperature type of structural change it is necessary for the

structure to have a thermal instability. In addition, it appears to be a fact beyond question that one is not permitted to make analogies with regard to crystal structures and physical properties based on criteria of behavior of a crystal under the action of radiation, since in the perovskite-like compounds PbTiO₃, PbZrO₃ and BaTiO₃ we find structural rearrangements in the two latter materials,¹³⁻¹⁷ while there is none of PbTiO₃¹³ although the properties of PbTiO₃ are closer to those of BaTiO₃.

After investigating materials like TiO₂, PbO, CaCO₃, SrCO₃ and BaTiO₃, and drawing on the literature data concerning α -SiO₂ and ZrO₂, the authors of Ref. 6 came to the conclusion that radiation-induced structural variations can be expected in crystals with displacement-type phase transitions and not reconstruction-type phase transitions. However, from the available data on K₂SO₄,⁶² and from the fact that one observes in n-irradiated Ca₂SiO₄ a transition from the monoclinic γ -phase to the heat-induced intermediate β -phase and not to the α -phase¹² although the structures of the β and α phases are close and the transition β - α is of displacement type, it follows that the presence of a transition of this type is not a necessary and sufficient condition for a radiation-induced transition.

In Ref. 15 it was concluded that for a rearrangement to take place it is important to have present some peculiarity of structure, for instance some sort of open channels which are oriented in a definite fashion, and which are capable of providing the required anisotropy in the unit-cell parameters. In all the crystals in which radiation-induced changes are observed, these parameters do in fact vary anisotropically. However, from the compounds investigated in that paper we can at least point to three materials—phenakite, beryl and topaz—in which the variation in these parameters under n-irradiation is extremely anisotropic, while there is no observed change in the crystallographic system although the structure of beryl is close to that of quartz while phenakite crystals have open channels parallel to the [001] axis. The

TABLE II. Changes in atomic positions for irradiated quartz.

α -quartz ⁵³		Irradiated α -quartz		β -quartz ⁵⁴
		3.5 × 10 ¹⁹ n/cm ²	4 × 10 ¹⁹ n/cm ²	
Si: <i>u</i>	0,4697 (2)	0,4752 (4)	0,4816 (7)	0,5
O: <i>x</i>	0,4125 (4)	0,416 (1)	0,419 (1)	0,4138
<i>y</i>	0,2662 (4)	0,260 (1)	0,252 (1)	0,2069
<i>z</i>	0,1188 (2)	0,1232 (7)	0,133 (1)	0,1667
Si—O (Å)	1,610	1,609	1,602	1,590
Si—Si (Å)	3,057	3,078	3,087	3,091

absence of a high-temperature type of rearrangement in topaz may be due to the fact that in this compound the thermal phase transition is not observed until $T = 1100^\circ\text{C}$ at which it decomposes into mullite and chrysotilite.⁶³ In beryl, however, the transition is observed; at roughly $T = 1200^\circ\text{C}$ the crystal is biaxial, which indicates structural changes.⁶⁴

With a goal of verifying the stated assumptions regarding conditions which are capable of giving rise to radiation-induced high-temperature types of structural rearrangement, there was presented in Refs. 17, 24 an investigation of the temperature dependence of x-ray diffraction effects over a wide temperature interval for single crystals of those compounds in which the presence of these rearrangements has been established (α - SiO_2 , KNbO_3 , BaTiO_3 , PbZrO_3). With just this goal in mind, the authors investigated the action of various types of radiation and heating for a number of specially-chosen single crystals (NaNO_2 , CsNO_3 , RbNO_3 , NaNO_3 , KNO_3 , NH_4Cl , K_2SO_4 , $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4$, SbNbO_4 , KH_2PO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$),^{20,21,27,65}

The experiments presented there lead to the conclusion that in order for radiation-induced rearrangements of high-temperature type to occur it is necessary that certain relations be satisfied between derivatives of the thermodynamic potential, which ensure the appearance in the unirradiated crystal of a phase transition of continuous type, or that the pre-phase transition regime extend over a wide temperature range.⁶⁶

Investigations show that in all the single crystals studied for which changes in structure of high temperature type are observed, the thermal phase transitions are of the above-mentioned type. The data obtained in Refs. 12, 18 also confirm this postulated criterion for radiation-induced instability. As was noted earlier, in irradiated crystals of Ca_2SiO_4 one observes a transition from the original γ -phase not to the ultimate heat-induced phase as takes place in KNbO_3 ,^{15,18} but to the intermediate β -phase,¹² corresponding to the fact that in CaSiO_2 the γ - β transition alone is spread out over a relatively wide temperature interval, whereas in KNbO_3 all the high-temperature phase transitions are transitions with quite sharply-defined pre-transition regimes.⁶⁰ Finally, for all the crystals chosen on the basis of having phase transitions of the above-mentioned type, the changes observed under irradiation, as the available data show, are qualitatively similar to those which are recorded in unirradiated crystals close to a phase transition in those cases where there is no clear evidence of decomposition of the original compound under the action of radiation.

It is especially interesting to compare data on the behavior of the isostructural low- and high-temperature modifications of CsNO_3 and RbNO_3 under the same conditions of γ -irradiation, as these compounds undergo transitions of different sorts under heating up to very similar temperatures ($T_{\text{PT}} \approx 150^\circ$ and 160°C). As opposed to CsNO_3 , in which the structural change in the modification on the high-temperature side is observed long in advance of reaching T_{PT} , in RbNO_3 crystals no noticeable change in the x-ray picture is observed even up to the appearance of reflections from nuclei of the high-temperature phase. Correspondingly, in γ -irradiated CsNO_3 crystals grown from solution on "seeds," distinct changes in crystal structure of high-temperature type are observed already for doses $\sim 10^8$ R, whereas in

RbNO_3 crystals radiation-induced rearrangement is not observed even for doses $\sim 10^{10}$ R, where already there appear clear indications of disruption of the strict periodicity of atomic positions. From these data one concludes unambiguously that in radiation-induced structural rearrangement the decisive role is played not by structural peculiarities of the crystal but by the character of the phase transition.

4. MODELS OF RADIATION-INDUCED STRUCTURAL STATES

From analysis of such characteristics of the defect structure as the form and orientation of point defect structures, and also from the position of defects relative to the original lattice, and a comparison of the dose and temperature dependences of the changes in the structural states, it follows that at the foundation of radiation-induced rearrangements lie general thermodynamic regularities which define the behavior of any metastable system, independent of the origin of the instability.

A comparison of the changes in irradiated crystals, in compounds with non-stoichiometric composition, and in solid solutions with various percentages of dissolved atoms, confirms this conclusion. Point defects or foreign atoms occupying specific types of structural positions are for small concentrations distributed randomly relative to each other. An increase in concentration leads to the appearance of correlation effects which favor regular arrangements of these defects, and consequently lead to a local change in the position of atoms of the original compound, until certain overall changes of structural type are observed; these changes are recorded both in non-stoichiometric materials and in solid solutions.^{69,70}

The form, orientational relations and positions of the clusters which are created at specific mobilities and concentrations of point defects of radiative origin also are subject to the sort of regularities which characterize solid solutions. Thus, the dependence on dose of the creation of anisotropic point defect clusters in irradiated AHCs (x-irradiated NaCl and n-irradiated LiF) reflects an analogy with the succession of processes observed in solid-solution compounds with impurities as the concentration of dissolved atoms increases, in which there occurs a precipitation of regions with other than the mean value of electron density, all identical in shape and orientation.

A calculation of the minima energy of decomposition of a ternary solution, taking into account elastic stresses,⁷¹ is as a general rule carried out by describing the form, orientation and position of nuclei of the new phase in the original alloy, and of clusters of point defects in irradiated,^{27,36,72,73} tempered⁷⁴ or deformed crystals.⁷⁵

In compounds which do not undergo a phase transition under heating, the crystal structure does not change even under irradiation, independent of the concentration of isolated point defects. However, in those compounds whose crystal structure is unstable and in which phase transitions are observed which are spread out over a wide interval, radiation can also give rise to structural rearrangements of high-temperature type. For specific doses of radiation, stable structural states form in these compounds which are qualitatively similar to states observed in unirradiated crystals in their pre-phase transition stages. It should be emphasized that these states are not completely identical, by virtue of a

number processes (principally amorphization and decomposition of the original compound) which as a rule accompany the radiation-induced structural rearrangement.

From the ensemble of available data we can conclude that as a basis for describing type I structural states at various stages of irradiation it is expedient to take solid solutions as a model, considering the point defects of radiative origin as dissolved atoms. The configurational change in structure of an irradiated crystal can be described with the help of the same model, taking into account correlation effects caused by the interaction of electric and elastic fields of point defects. In devising a model of radiation-induced structural rearrangement of high-temperature type for such compounds as α -SiO₂, KNbO₃ and BaTiO₃, we can treat the directional static atomic displacements due to primary defects as similar to displacements of dynamic character.

5. INFLUENCE OF IMPURITIES, GROWTH CONDITIONS AND IRRADIATION CONDITIONS ON THE RADIATION HARDNESS OF A STRUCTURE

The investigations and analysis of available results presented here lead us to conclude unambiguously that the quantities which are decisive in forming all types of radiation-induced states, including also structural crystal rearrangements, turn out to be the concentration of point defects of radiative origin and their mobility; these quantities are determined primarily by dose, irradiation temperature and self-diffusion coefficients. From published work (essentially on metals and semiconductors) it follows that impurities can also affect significantly the behavior of the primary defects and their interactions.

No systematic investigations have been carried out on how the above-mentioned factors can influence the creation of structural states in irradiated crystals. With regard to the mechanism by which these states form in crystals with ionic-covalent bonds, the most interest centers on study of how impurities and defects of non-radiative origin perturb the stability of the crystal structure against irradiation. This interest is explained by the fact that existing disagreements regarding the variation in defect structure are practically eliminated if we take into account the irradiation temperature of the crystal, whereas there is no unanimity of opinion regarding the mechanism of structural rearrangement. Certain investigators assume that the high-temperature rearrangements observed in crystals can be treated as ordinary thermal phase transitions which are taking place at a lower temperature T_{irr} , since for a number of these crystals a lowering of T_{PT} is recorded under the action of radiation.^{11,13,76-80} However, investigations of the temperature dependence of diffuse scattering by neutron-irradiated single-crystal quartz,^{9,10,43} and the results of Refs. 10, 20, 21, 27 and 81, force us to conclude that this picture cannot correspond to the real situation. In point of fact, the high-temperature rearrangement for this series of compounds is not mediated by a nucleation mechanism, but rather is due to the introduction of radiation-induced point defects which give rise to correlated atomic shifts which are static in character.^{10,27,81-83} In addition, there are significant differences of opinion in connection with the doses at which the rearrangement occurs, and there is no unanimity of opinion^{13,15} even with regard to the very existence of a change in crystal structure in some compounds.

Investigations of the influence of growth-induced defects and impurities on the character and temperature of the phase transition in unirradiated crystals have been carried out with considerable intensity within the last seven years. Data on the way these imperfections affect radiation-induced rearrangement of the crystal structure were published for the first time in 1981.^{84,88} We will analyze the results of investigations of the relationship between dose and temperature and variation of structure, taking into account the influence of impurities (α -SiO₂), variations in growth conditions (CsNO₃) and changes in irradiation conditions which determine the activity with which diffusion processes take place (NaNO₂), i.e., those factors which determine the total concentration of radiation-created isolated point defects.

5.1. Dependence of the kinetics of radiation-induced rearrangement of crystal structures on impurity content

The choice of quartz as an exemplary medium in which to study the influence of impurities on an irradiated crystal structure is an obvious one, since the regularities and mechanism by which a radiation-induced high-temperature type of rearrangement is formed are most fully studied for single crystal α -SiO₂. Of no small importance is the fact that the processes of amorphization and decomposition of the original compound, which compete with the processes which tend to rearrange the crystal structure, only rarely interfere with the reliability with which we can establish the presence of a structural rearrangement and study the dose dependence of the observed changes (one case of such interference, however, is for n-irradiated α -SiO₂).

Results relating to the effect of neutrons on specially-grown single crystal quartz with a controlled quantity of structural impurities of substitutional type (Al, Ge) show convincingly that the radiation-induced high-temperature type of structural rearrangement is wholly determined by the total concentration of point defects of radiative origin.⁸⁷

Investigations were carried out on natural-crystals originating in Volynsk, on single crystals grown by the method of hydrothermal synthesis with a minimal quantity of impurities ($\leq 10^{-4}\%$ by weight), and on crystals specially doped with aluminum and germanium. After radiation doses of $\sim 10^{19}$ n/cm², noticeable changes in crystal structure which tended to approach the high-temperature modification were observed to appear only when the irradiated crystals had minimum impurity content. This conclusion was arrived at both from a comparison of the intensities of Laue and Bragg maxima and from analysis of the intensity distribution of x-ray diffuse scattering before and after irradiation.

Clearly-defined changes are observed in the relations between the intensity of the diffraction maxima only in the purest samples, for which the changes which occur are close to those which are characteristic of an initial pre-phase-transition stage, and correspond to heating unirradiated native crystals up to $T \approx 500^\circ\text{C}$ and up to $T \approx 350^\circ\text{C}$ for crystals with minimum impurity content. The results of an analysis of the diffuse-scattering intensity are in good agreement with the estimates presented above (Fig. 7). Changes in the distribution J_{diff} in the purest samples after doses of $\sim 10^{19}$ n/cm² practically coincide with changes caused by heating a native crystal up to $T = 500^\circ\text{C}$, and are close to the distribu-

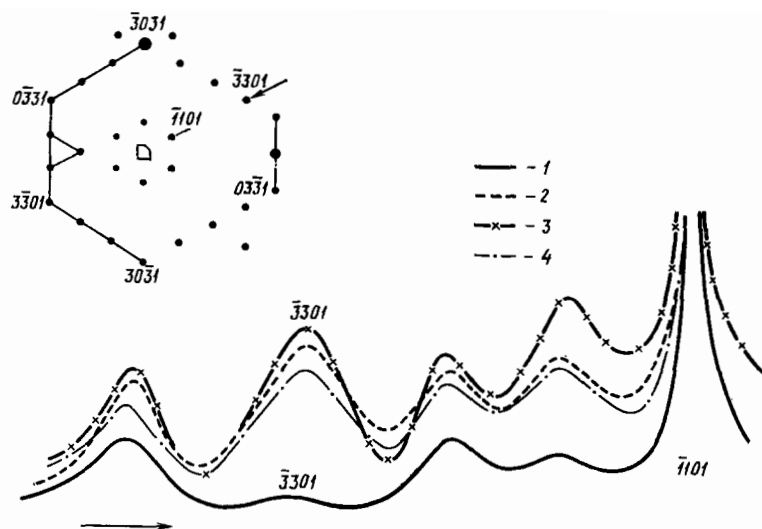


FIG. 7. Intensity distribution of diffuse scattering of K_{α} Mo x-rays for quartz crystals with various impurity concentrations. I—Al, Ge, Fe $\sim 10^{-4}$; II—native quartz: Al $\sim 5 \times 10^{-2}$, Fe, Li $\sim 2 \times 10^{-3}$; III—Al $\sim 5 \times 10^{-2}$, Ge, Fe $\sim 10^{-4}$; IV—Ge $\sim 9 \times 10^{-1}$, Al, Fe $\sim 10^{-4}$ by weight. 1—intensity in reduced units for $T = 20^\circ\text{C}$ for unirradiated crystals (I–IV) and irradiated (II–IV) ($F \sim 10^{19}$ n/cm 2 , $E > 0.5$ MeV, $T_{irr} \sim 150^\circ\text{C}$); 2—I, irradiated under the same conditions; 3—irradiated native crystals ($F \sim 3.5 \times 10^{19}$ n/cm 2 , $E > 0.5$ MeV, $T_{irr} \sim 150^\circ\text{C}$); 4—unirradiated native crystals, $T = 500^\circ\text{C}$.

tion of J_{diff} observed in native crystals of quartz after irradiating them with a dose $\sim 3.5 \times 10^{19}$ n/cm 2 .

The increased sensitivity of crystals with minimal impurity content to the action of radiation is confirmed by data on the determination of structural parameters by the diffractometer method and by an estimate of the change in macroscopic density measured using the method of "weighing" samples in a thermal-gradient pipe.⁹⁰ For these crystals, the change in position of the atoms towards the high-temperature modification side already exceeds the measurement errors⁸⁸ at doses of $\sim 10^{19}$ n/cm 2 , whereas for native crystals a noticeable high-temperature type of structural rearrangement is observed for doses $> 3 \times 10^{19}$ n/cm 2 (Refs. 8, 10, 81). The difference in density change for a dose of $\sim 10^{19}$ n/cm 2 is roughly a factor of 3: $(\Delta\rho/\rho)_i = 0.013$; $(\Delta\rho/\rho)_n = 0.004$.

Results on the change of atomic positions, intensities of diffraction maxima and the magnitude and distribution of J_{diff} in irradiated crystals with various impurity contents are extremely important both in determining the reconstruction mechanism and for possible applications. They take on special value when we take into account data on estimates of the dependence of the increment to J_{diff} on the spacing of sites in reciprocal space; this data is taken from irradiated single crystals⁸⁸ with minimal impurity content at doses $\sim 10^{19}$ n/cm 2 . Just as in the case of samples of native quartz with clearly-defined radiation-induced structural rearrangements of high-temperature type, it is found that $\Delta J_{diff} \sim 1/q^2$. On the basis of the calculations presented in Refs. 91–94, this dependence allows us to conclude unambiguously that the observed increase in the diffuse-scattering intensity is caused by point defects and not by clusters of them.

A number of very interesting and promising conclusions follow from the ensemble of available data on this topic. First of all, structural impurities, in interacting with the primary radiation-induced defects (essentially vacancies), reduced their concentration, which correspondingly increases the stability of the crystal structure against the action of radiation. Secondly, the data convincingly show that for neutron irradiation the rearrangement of the crystal structure does not come about by way of formation of high-

temperature-phase nuclei, and that the parameter which describes the instability of irradiated structures against transformation to the high-temperature modification is the concentration of isolated point defects of radiation origin. Besides this, the results obtained are of interest from the point of view of controlling the radiation hardness of crystal structures, and allow us to understand the cause of the observed discrepancies in estimating the doses needed to rearrange the structure of the same material.

Data on the investigation of single crystals of SbNbO_4 irradiated by electrons also demonstrate convincingly a clearly-defined dependence of radiation hardness of crystal structure on impurity content.^{65,88}

5.2. Influence of growth- and deformation-induced defects on structural changes in irradiated crystals

Crystals of cesium nitrate are the most convenient systems for investigating the dependence the radiation hardness of a crystal structure on its original degree of crystallinity. The compound CsNO_3 is the only one in which a structural rearrangement can be brought about easily under the action of γ - and x-irradiation at temperatures $< 40^\circ\text{C}$ while not leading to the formation of a "displacement zone."⁶¹ In addition, single crystals of CsNO_3 can be grown in various ways from sufficiently pure ingredients; all these things make it possible for us to eliminate the effect of other factors which determine the total concentration of point defects of radiative origin for a given radiation dose.

In order to investigate the influence of the original structural states on the high-temperature type of structural rearrangements observed in irradiated crystals of CsNO_3 , single crystals were studied as well as polycrystalline samples obtained by pulverizing single crystals grown by various methods.^{21,45,84,85} The most fully investigated samples were γ -irradiated single crystals grown from solution on a seed and obtained by spontaneous crystallization.

The study was carried out by diffractometer methods in conjunction with the Laue method. It should be noted that although the possibility of using the latter method is limited, it is the only method which allows us to obtain information about the effect of growth-induced defects on the behavior of

crystals under irradiation in their pure form, since in preparing the sample for diffractometer study the mechanical processing of single crystals causes defects of deformation origin. These defects can wholly mask out the radiation-induced structural changes in crystalline films.

Results for crystals of CsSO_3 grown by various methods and under various growth conditions show that growth-induced defects and defects originating from deformations introduced while preparing single crystal samples of a given size and shape, and also in grinding up the single crystals, turn out to have an important effect on the character and dose dependence of the radiation-induced changes in crystal structure. The differences which appear in the original structural states and the radiation hardness, as chemical analysis shows, are not related to differences in impurity content.

The effect of growth-induced defects on the radiation hardness of the structure of a crystal in its pure form is clearly observed in single-crystal samples undeformed by being worked on. Under the action of γ -irradiation a change in crystal structure of high-temperature type takes place in these crystals from the trigonal to the cubic modification; in more perfect crystals grown from seed a noticeable change in the direction of the high-temperature modification appears at doses $\sim 10^8 \text{ R}$,²¹ while for crystals obtained by spontaneous crystallization no noticeable change in the diffraction picture is observed up to doses $\sim 10^9 \text{ R}$.⁸⁴ At this dose level, the structure of crystals with a higher degree of perfection already corresponds to the symmetry of the cubic modification, whereas the structural rearrangement in less perfect crystals is still far from being completed even at a dose of $\sim 3 \times 10^9 \text{ R}$.^{21,45}

The processes of polygonization, which lead to fragmentation of irradiated samples, interfere with tracking the influence of the original structural states on radiation-induced changes in the structure of single crystals at higher doses.^{21,46,84} Changes in crystal structure, which are apparent at doses of radiation $\sim 2\text{--}9 \times 10^9 \text{ R}$ in pulverized single crystals of CsNO_3 , also are very strongly masked by defects originating from deformations due both to sample preparation and to processes which compete with the processes of structural rearrangement, e.g., formation of large clusters of point defects and decomposition of the original compound.^{27,85} Nevertheless, from the data presented in Ref. 85 we are led to the conclusion that, just as in the case of crystal processing methods which do not include deformation, the least stable structures appear in the most perfect crystals, although we can track the dose dependence of the change in crystal structure only in unprocessed single crystals.

By carrying out these investigations, we can demonstrate that growth- and deformation-induced defects, as well as structural impurities in quartz, can "capture" the radiation-induced defects. This effect can be used to induce controlled changes in the radiation hardness of crystal structures. In addition, we are led to a second conclusion, which has fundamental value for investigating the dose dependence of crystal structure rearrangements: in selecting compounds for investigating radiation-induced structural instability it is necessary to take into account not only the character of the phase transition and the strength of the interatomic interaction, but also the mechanical characteristics of the material (such as its plasticity and brittleness). The results obtained

also help us to understand the causes of discrepancies in experimental data reported by various authors on the action of radiation on crystal structures.

The influence of processing and growth conditions on the original state of the crystals is clearly illustrated by the differences in their properties and the appearance of anomalies in the temperature dependence of structural characteristics and properties of the same material (such as unit-cell parameters, dielectric permittivity, heat capacity, etc.).⁹⁵⁻⁹⁹

5.3. Changes in structure for differing dose sequences

From the point of view of investigating criteria, mechanisms and kinetics of the high-temperature type of crystal structure rearrangement, NaNO_2 is one of few compounds which satisfy all the necessary requirements both from the point of view of thermodynamic and mechanical characteristics and from estimates of the strength of the interatomic interaction.

As with CsNO_3 , in crystals of NaNO_2 the high-temperature type of structural rearrangement occurs under the action of γ -rays; however, in contrast to CsNO_3 the deformation-induced defects which arise in grinding larger single crystals of NaNO_2 into powder and separating the decomposition products in practice do not mask out the features of the rearrangement even up to doses $\sim 9 \times 10^9 \text{ R}$.^{86,88,7)} This allows us to track in detail the influence of radiation-induced annealing on the formation of structural states over a sufficiently wide interval of dose, since effects due to γ -irradiation are clearly evident even for doses $\sim 2 \times 10^9 \text{ R}$.^{20,65} These effects are manifest in a sharply-defined change in the relation between the intensities of diffraction lines in the direction of the high-temperature modification. As the dose increases up to $\sim 4 \times 10^8 \text{ R}$, the effects become more obvious, and there is no longer any reason to doubt that the dose dependence of the intensity has the same features as for the case of heating (Fig. 8).

In studying the structural changes at these large doses it is expedient to proceed by taking into account the influence of irradiation conditions, since the basic parameter which drives structural instability of irradiated crystals—the concentration of point defects—is determined both by the activity of formation of defects in the process of irradiation and by

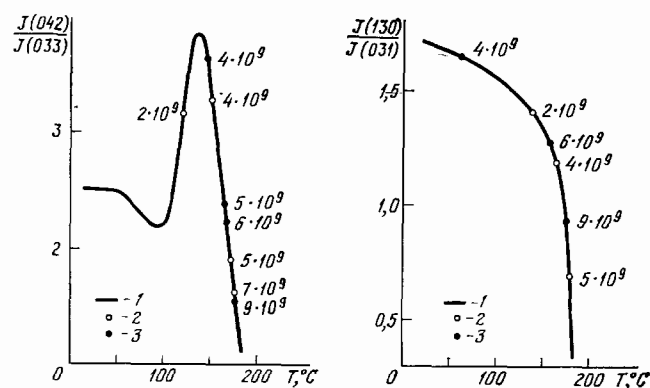


FIG. 8. Dose and temperature dependence of the ratio of the intensities of Laue maxima for crystals of NaNO_2 . Doses are shown in roentgens, 1—unirradiated, 2,3—initial doses $< 2 \times 10^9 \text{ R}$ (2), $\sim 4 \times 10^9 \text{ R}$ (3).

the radiation-induced annealing. The latter depends on the properties of the material itself and on the irradiation conditions, above all the irradiation temperature, which directly influences the rate of diffusion processes and thus determines the procedure of dose selection, because the annealing begins to occur actively when the concentration of point defects attains a specific concentration.^{27,41}

As is clear from Fig. 8, the possibility of varying T_{irr} is very limited, since a significant change in the structure of NaNO_2 upon heating is recorded starting at a very low temperature. Therefore, with a goal of studying the effects of radiation-induced annealing on the kinetics of rearrangement, in Ref. 86 crystals were studied which were irradiated using various methods to attain the total dose. Polycrystalline samples of this material were irradiated by γ -rays both continuously and in several stages with intermediate long-period annealing at room temperature.

From the data presented in Fig. 8 on the influence of irradiation and heating on the crystal structure of NaNO_2 we can conclude that the dose dependence of the structural states created by irradiation depends essentially on the method of dose delivery one sees a clear shift toward the low-temperature regime in the change in the structure of crystals irradiated with initial doses $> 2 \times 10^9$ R. These same conclusions follow from analysis of the positions of the diffraction lines, which reflect the change in unit-cell parameters.^{86,88}

From the results presented and published in Refs. 27, 41 we can conclude that starting at certain irradiation doses one observes activation of the diffusion processes leading to radiation-induced annealing of the primary defects. The available data on the influence of condition of dose delivery on the formation of total structural states is of undoubted interest, since it is a confirmation of the decisive role of point defects in radiation-induced rearrangement of the crystal structures of irradiated crystals.

As regards the influence of radiation-induced annealing on the formation of a global defect structure for a given radiation dose we can judge by the data presented in Section 2.

6. CONCLUSION: FACTORS WHICH DETERMINE THE STRUCTURAL STATES OF IRRADIATED CRYSTALS

The study of regularities which characterize the action of radiation on crystals with various types of interatomic bonds has a very significant value not only for analyzing the radiation hardness of crystal structures but also for fixing and enhancing the physical properties of a given material over a given temperature interval, and obtaining fundamentally new structural states (and consequently new properties) under the action of irradiation.

From an analysis of the totality of available results concerning the action of radiation on crystals with ionic-covalent bonds, there follow definite conclusions and recommendations for realization of a given state. It is obvious that the basic factors which determine the overall radiation-induced structural state at any given level of irradiation are the thermodynamic and mechanical characteristics, interatomic bonds, impurity content, degree of perfection of the crystal under study and the irradiation-dependent migration mobility of defects and their surrounding atoms.

The conditions for formation of complexes and clusters of point defects can be created by choosing the type of radi-

ation, the dose and the irradiation temperature. The character of secondary defects depends on the distribution of primary defects throughout the volume, and consequently on the mechanism of their formation and on their migration mobility, which is determined (taking into account the activation of diffusion processes in irradiated crystals) by dose, temperature and the self-diffusion coefficient. The average size distribution of secondary defects and the concentration ratios between primary defects and secondary defects of various types depend on the type of radiation, the irradiation temperature, the dose, the magnitude of the flux and the self-diffusion coefficient. The shape of the secondary defects, their orientational relationship with the lattice of the original crystal and regularities in their location in the volume are the same for all types of irradiation. The kinetics of defect formation are determined basically by dose, temperature of irradiation and the original defect structure. By varying the irradiation conditions we can change the defect structure of a crystal and its type of structural state in a controlled way.

In order to change the stable equilibrium positions of atoms and subsequently to rearrange their structure beyond the fixed limitations imposed by the restrictions of thermal stability of the crystal structure and its thermodynamic and mechanical characteristics, it is necessary either to create conditions which ensure the presence of isolated point defects over a wide dose interval or to generate a region (of "displacement zone" type) which is convenient for creation of stable nuclei of the new phase.

For the majority of compounds which have been studied, the parameter which drives the high-temperature type of radiation-induced instability of a crystal structure is the concentration of point defects of radiative origin. Consequently, due to the change in all the factors which influence this parameter—dose, radiation-induced annealing, impurity content and original defects of specific type—we can direct and control the kinetics of the rearrangement and ultimately the overall radiation hardness of the structure. In addition, taking these factors into account allows us to set up conditions for formation of practically any metastable structural state which is stable at room temperature, and which is similar to some state which appears at some pre-phase-transition stage of the unirradiated crystal.

From analysis of the data presented above we conclude that radiation-induced rearrangement, amorphization and decomposition of the original compound are all competing processes whose activity depends on the irradiation temperature and the strength of the interatomic interaction. Lowering the temperature leads to a slowing of the decomposition and suppression of the accompanying crystal deformation, which is of special significance for realizing and isolating structural changes in irradiated crystals which do not possess sufficient brittleness.

Taking into account conditions of irradiation, especially temperature, dose and the energy spectrum of the radiation, and also impurity content and original defect structure, allows us to understand the causes of discrepancies in experimental data on the same material, and differences in their interpretation.

¹¹It has been established from results obtained at the present stage of investigation on the influence of radiation on non-metallic crystals that, besides amorphization and decomposition of the original compound,

- changes in crystal structure have been reliably observed: in n-irradiated crystals of ZrO_2 (Refs. 1-4) (when a specific concentration of fission fragments is reached), SiO_2 (Refs. 5-11) (quartz and cristobalite), Ca_2SiO_4 ,¹² $PbZrO_3$,^{13,14} $BaTiO_3$,^{13,15-17} $KNbO_3$,^{15,18} in $CmAlO_3$ (Ref. 19) (under the action of particles from radioactive decay), in γ -irradiated crystals of $NaNO_2$ (Ref. 20) and $CsNO_3$ (Ref. 21) under the action of γ - and x-rays. We should stipulate that in this group we do not include intermetallics, e.g., U_3Si (Ref. 22) and complex rare-earth compounds such as the solid solution of Dy_2O_3 in $Dy_2Ti_2O_7$,²³ in which one clearly observes structural changes at a definite stage of n-irradiation.
- ²Reciprocal space is introduced in order to interpret x-ray scattering conveniently by using a wave-vector (or momentum) space in which harmonics are displayed as a linear sequence of equivalent points.
- ³In n-irradiated single crystals of NaCl and KCl anisotropic clusters do not form even for doses $\sim 5 \times 10^{18}$ n/cm².
- ⁴The formation of stable planar vacancy clusters with thicknesses of about one interatomic spacing is possible only when they are filled by atoms of gaseous decomposition products.
- ⁵The technique employed in Refs. 27, 28 allows us to measure the magnitude of J_{diff} and analyze the dependence $\Delta J_{diff} = f(q)$ in that region of reciprocal space which yields information on point defects and clusters of point defects with sizes 40-70 Å.
- ⁶A "displacement zone" is a region consisting of atoms randomly displaced from their stable equilibrium positions, which appears in a crystal when the energy of fast particles is transferred to the crystal in the course of slowing down.
- ⁷It is not possible to conduct an investigation of the dose dependence of the structural changes in single crystals of $NaNO_2$, since the deformation processes which accompany the irradiation and which are caused by decomposition of the original compound lead to mechanical destruction of single-crystal samples. Accordingly, comparisons of the temperature and dose dependences are carried out by diffractometer methods on polycrystalline samples.^{20,65,66}
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