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Influence of Impurities, Irradiation and Temperature on the Mechanical and Electrical Properties of LiF Crystals

On the basis of study of the temperature dependence of mechanical and electrical properties of LiF crystals with different impurities an evident interaction between radiation defects and impurities is revealed. As a result of trapping of radiation defects (F- and H-aggregate colour centres) by impurity centres the reconstruction of impurity centres takes place, causing a change of mechanical and electrical properties.

На основании изучения температурной зависимости механических и электрических свойств кристаллов LiF, различающихся примесным составом, выявлен характер взаимодействия радиационных дефектов с примесями. В результате захвата примесными центрами радиационных дефектов (F- и H-агрегатных центров окраски) происходит престройка примесных центров, что влечет за собой изменение механических и электрических свойств.

1. Introduction

In the investigation of the dependence of a number of physical properties on the dose of γ-irradiation of LiF crystals differing in concentration of oxygen the existence of critical doses was revealed. At these doses drastic changes in the properties occur due to the change of the dominant type of radiation defects. At the same time it is known that there exist critical temperatures at which significant transformations of radiation defects and impurity centres occur (CATLOW et al; SARKÖZI, PREDVODITELEV) Models of a successive reconstraction (aggregation and recombination) of radiation defects in alkali halides under the influence of temperature increase were developed by CATLOW et al. Besides the dose of irradiation and subsequent heat treatment of crystals, the nature and state of radiation defects are influenced by impurities in crystals (URUSOVSKAYA, KNAB). Comparing the change with temperature of physical properties of irradiated and non-irradiated crystals of different constitution one can reveal the role which defects introduced by irradiation play in the reconstruction of the impurity centres under the influence of temperature. Such investigation has been carried out in the present work for one radiation dose $1.5 \cdot 10^5$ J/kg corresponding to the beginning of aggregation of F- and H-centres. We judged indirectly about the reconstruction of impurity and radiation centres at high temperature by the change of mechanical and electrical properties.

2. Experimental methods

The objects for investigation in the present work were LiF I and LiF II crystals. The two types of crystals contained the same background impurities (Mo, Ca, Al with the total concentration 10^{-4} wt%) and differed in the oxygen content. In LiF I crystals grown by Stockbarger method in vacuum oxygen was not revealed while in LiF II crystals oxygen was introduced into the melt (as Li_2O) and the crystals were grown in the air by Kyropulos method.

Mechanical properties were estimated by yield point (τ_I) and the stress corresponding to the beginning of the stage of deformation recovery (τ_{III}). Besides, we paid attention to the shape of deformation curves. These curves were obtained during uniaxial compression of cleaved specimens on the "Instron" testing machine. The deformation rate was 10^{-4} s^{-1}, temperature varied from room temperature to 773 K.

Electrical characteristics (electroconductivity) were measured in the same temperature interval. The measurements were made at direct current according to a three-point scheme at field strength 1000 V/cm.

3. Experimental results

3.1. Stress-strain curves

Figures 1 and 2 show typical stress-strain curves of the investigated crystals at different temperatures. The presence of oxygen, irradiation and temperature is seen to

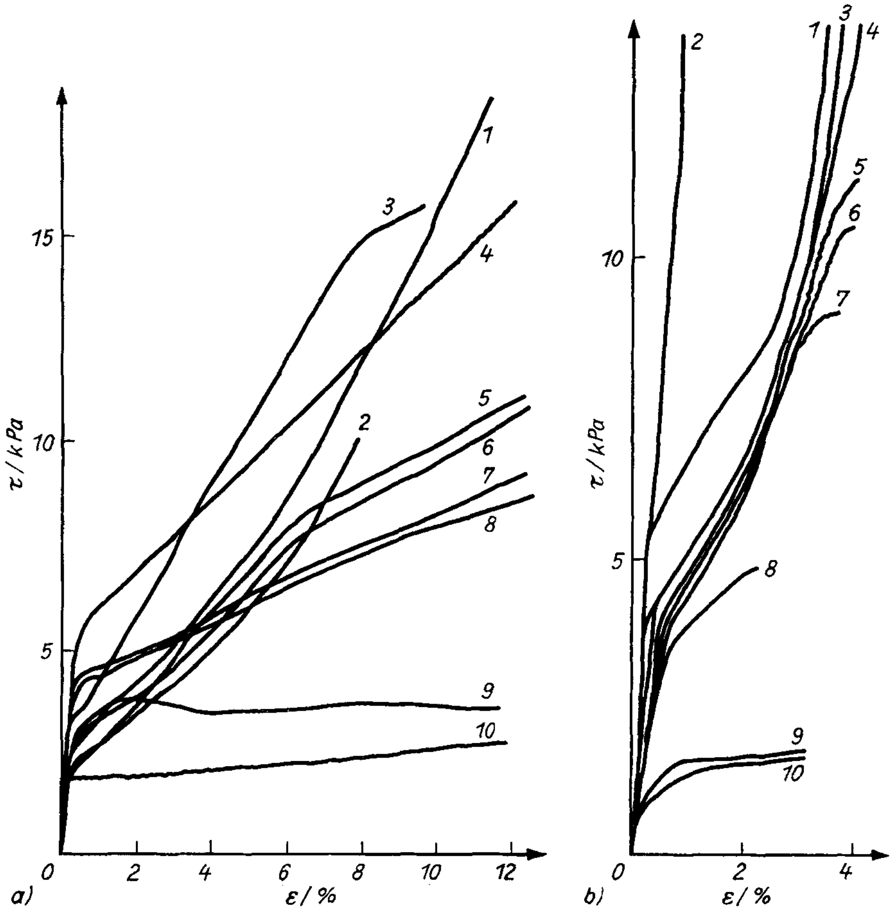

Fig. 1. Stress-strain curves for LiF I crystals, obtained at different temperatures: 1 300 K, 2 373.K, 3 473 K, 4 523 K, 5 573 K, 6 693 K, 7 633 K, 8 673 K, 9 723 K, 10 773 K (a before γ-irradiation, b after γ-irradiation)

exercise significant influence on these curves. Firstly, the oxygen removed a threestage character of deformation (In LiF I the three stages are preserved up to 673 K). Secondly, the oxygen increased the tendency to serrated yielding (jerky flow), broadening, towards high temperatures, the interval of serrated yielding and increased the amplitudes of jumps.

At room temperature LiF II crystals have a little bit lower yield point than LiF I, however, LiF II crystals have a lower total plastic deformation: for LiF I it is not less than 18—20% while for LiF II it does not exceed 6—8%. Increase in brittleness in LiF II is the cause of absence of three stages of work hardening, i. e. the strength limit is lower than the stress of beginning of II deformation stage. With the increase in temperature the stress-strain curves change their shape. The first and second stages become shorter and the stresses, corresponding to the beginning of all the three stages, become nearer to each other. Simultaneously, the inclination of all the stages is reduced. At the highest testing temperature (773 K) the stages are absent and after reaching the yield point, the deformation proceeds without hardening and sometimes with a negative hardening (for example, in LiF I at 713 K). Starting from 673 K the limiting plastic deformation increases.

Irradiation also exercised influence on stress-strain curve (Fig. 2a and b) making the three stages in LiF I more distinct and introducing the three- stage deformation

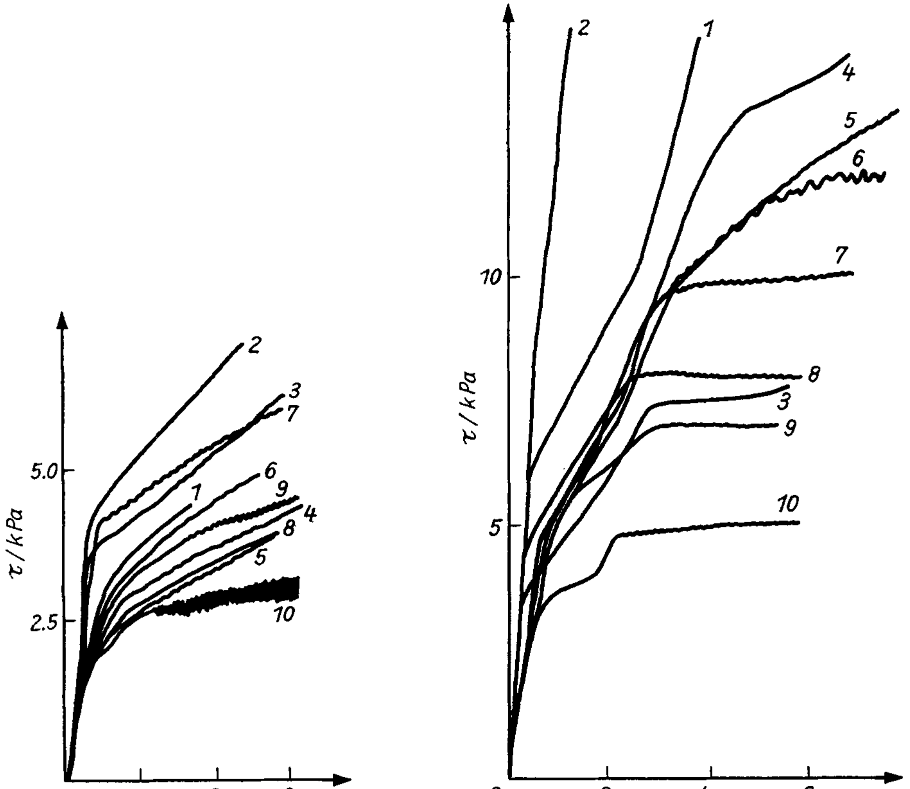

Fig. 2. Stress-strain curves of LiF II crystals, obtained at different temperatures (designations are the same as in Fig. 1)

in LiF II at all temperatures studied. The temperature interval of jerky flow for both crystals becomes a little bit narrower and the maximal in amplitude jumps were observed at lower temperatures. Such an influence is especially strong for the curves of LiF II. Irradiation changed the limiting plastic deformation of LiF I and LiF II differently: in the first case the crystals become more brittle, and in the second case — more plastic, that is why three stages appear after the irradiation.

3.2. Temperature dependence of yield point

Figure 3 shows the dependence $\tau_I(T)$ for LiF I and LiF II before and after irradiation. First of all, a non-uniform change of mechanical characteristics is seen. In all the cases there are maxima and minima. The oscillations of yield point of irradiation and non-irradiated specimens of LiF I occurs in antiphase except for a region of $\tau_I(T)$ above 673 K. The maxima and minima on the temperature dependence of mechanical properries are due to the periodic reconstruction of the impurity complexes

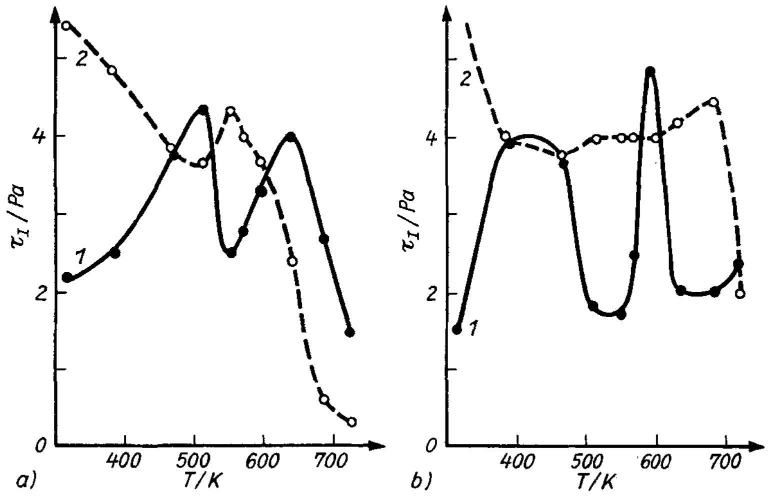

Fig. 3. Temperature dependence of the yield point of LiF I (a) and LiF II (b): 1 before γ-irradiation, 2 after γ-irradiation

(BRENNER, KRONMÜLLER) — the formation of one type of complexes with their successive decomposition and the formation of other complexes including impurities and intrinsic point defects. The antiphase oscillation of the characteristics of irradiated and non-irradiated crystals means that radiation defects either inhibit the formation of impurity complexes typical of the non-irradiated state (radiation defects interact with impurities) or assist the dislocations to overcome them. Both cases are possible.

Two maxima are seen on $\tau_I(T)$ at 523 K and 673 K in LiF I crystals. After doping with oxygen there is observed a shift of maxima towards lower temperatures and a change in peaks width on the temperature dependence τ_I.

Radiation defects influence the structure of all impurity centres, destroying the pre-radiation impurity centres and creating others with another stability region as compared to that of post-radiation impurity centres. It is seen that in LiF II the irradiation, to some extent, nullifies the influence of both cationic and anionic impurities (an almost horizontal segment of $\tau_I(T)$ curve in the wide temperature interval 373—673 K), i. e. in LiF II the irradiation has stabilized mechanical properties at these temperatures.

3.3. The temperature dependence of the stress, corresponding to the beginning of deformational recovery

Figure 4 shows the dependence $\tau_{\rm III}(T)$ for both LiF I and LiF II before and after irradiation. There is quite a remarkable decrease (25–30 times) in $\tau_{\rm III}$ after the heating of LiF I up to 773 K. The general exponential behaviour is complicated by two maxima. These maxima are at the same temperatures 523 K and 673 K as peaks of $\tau_{\rm I}(T)$. It means at the same temperatures there is an increase in yield point as well as inhibition of the deformation recovery. The dependence $\tau_{\rm III}(T)$ in LiF II after irradiation is shown in Figure 4b. It is seen that in temperature interval 400–600 K the deformation recovery proceeds at lower stresses than in LiF I before and after irradiation. It means that in the presence of oxygen there is bigger number of single point defects favouring the recovery under load.

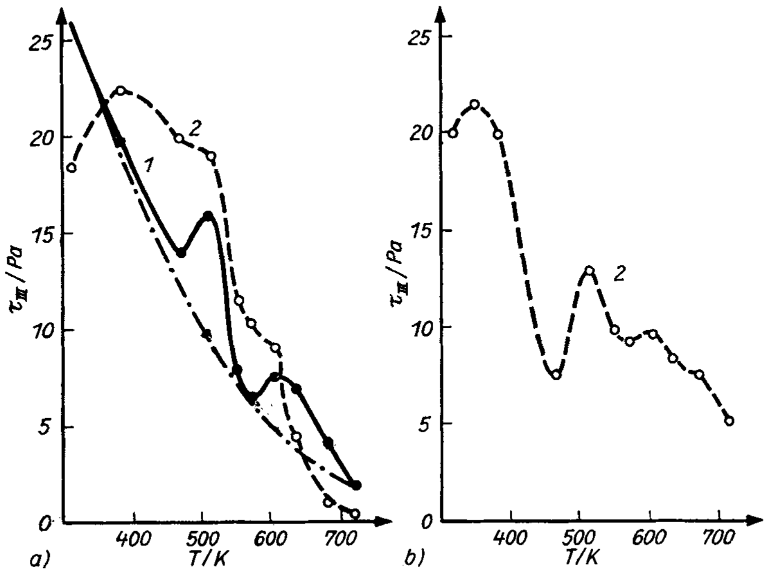

Fig. 4. Temperature dependences of the stress, corresponding to the beginning of the deformation recovery stage for LiF I (a) and LiF II (b): 1 before γ-irradiation, 2 after γ-irradiation; dashed line •—•—• — theoretical line (exponenta)

3.4. Temperature dependence of the electroconductivity

The plots lg $\sigma(1/T)$ for LiF I and LiF II are shown in Figure 5. The high value of σ for LiF I crystals is due to the presence of "background" impurities, forming impurity-vacancy dipoles $\mathrm{Me^{2+}V_c^-}$. By the temperature dependence of ionic conductivity of LiF I one can estimate the concentration (x_i) of non-predictable metallic impurity in a solid solution. This is done by extrapolation of the curve lg σ $(1/T)$ in the region of intrinsic as well as extrinsic non-associated conductivity to $1/T \rightarrow 0$. For LiF I $x_i = 1.5 \cdot 10^{-7}$ mole/mole, i. e. $7 \cdot 10^{15}$ cm^{-3} of the sites in LiF lattice is occupied by a bivalent impurity, its extra charge being compencated by cationic vacancy.

The values of the activation energy of conductivity in different temperature intervals for LiF I and LiF II are listed in Table 1. According to the experimental values of E and the published data about the mobility of carriers as well as binding energy of $\mathrm{Me^{2+}V_c^-}$ and $\mathrm{V_c^-V_a^+}$ complexes in "pure" and oxygen doped LiF crystals (Vora et al.;

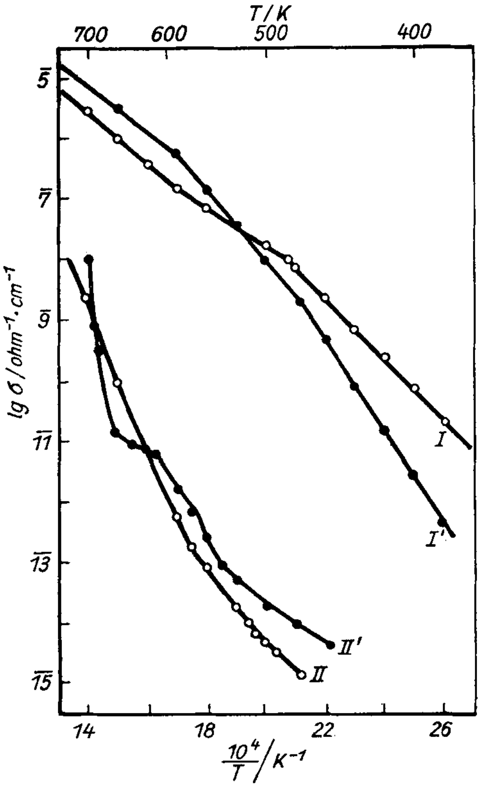

Fig. 5. Temperature dependence of ionic conductivity of LiF I (curves I and I′ for non-irradiated and irradiated crystals, respectively) and LiF II (curves II and II′)

Table 1

Activation energy of intrinsic conductivity of LiF I and LiF II crystals for different temperature intervals (eV).

Error of the estimation ±0.03 eV, I, I′ and II, II′ data for LiF I and LiF II before and after γ-irradiation, respectively, dose $1.5 \cdot 10^5$ J per kg. Numbers in square brackes — the corresponding temperature interval (K). Numbers in round brackets — binding energy of the corresponding to the given temperature intervals impurity-vacancy or vacancy complexes.

	Associationless conductivity	association conductivity	
	E_1	E_2	E_3
I	[203 – 588] 0.75 V_c^-	[588 – 473] transisition region	[473 373] 0.95 (0.4)$Me^{2+}V_c^+$
I′	0.75 V_c^-	1.15 (0.8)$V_c^-V_a^+$	1.55 $Me^{2+}V_c^-X_2^-$
II		[773 – 573] 2.12 $V_c^-V_a^+O^{2-}$	[573 – 503] 1.35 (0.8)$V_c^-V_a^+$
II′	[703 – 620] non-linear behaviour	[620 – 567] 1.38 ($V_c^-V_a^+$)	[567 – 453] non-linear behaviour

Bauer et al.; Stoebe; Rozman) one can conclude that the charge is transported by the displacement of V_c^- originated by decomposition of impurity-vacancy dipoles and divacancies.

Due to the presence of oxygen in LiF II there is a drastic lowering of conductivity level (Fig. 5, curve II). On the dependence lg σ $(1/T)$ of this crystal there is no segment due to dissociation of $Me^{2+}V_c^-$ complexes as well as no segment due to associations but there appears a segment due to vacancy pairs ($E = 1.35$ eV). The lowering of conductivity due to oxygen can be explained, first, by compensation of the extra charge of the background impurity (according to X-ray spectra analysis the content of metallic impurity in LiF I and LiF II is approximately the same) by the charge of O^{2-} ion itself and by the formation of complexes MeO or $Me(OH)_2$, causing a relative reduction of concentration of extraequilibrium cationic vacancies. Second, the total or partial dissociation of a $O^{2-}V_a^+$ assisted not only the appearance of free V_a^+ but also the formation of $V_a^+V_c^-$ pairs, which reduced further the conductivity of LiF II crystals.

At temperatures 573—773 K there is a segment on the curve with $E = 2.12$ eV. This value is close to the activation energy of the charge transport in the region of intrinsic conductivity ($E = 2.07$ eV (Mariani; Vignolo), when both cations and anions are carriers. The presence of a segment with such a high activation energy in the association conductivity interval can be connected with the presence of rather complex and quite stable aggregate defects, including V_c^-, V_a^+ and oxygen ions, in the crystals.

The irradiation significantly changes the dependence lg $\sigma(1/T)$. In LiF I at temperatures above 523 K there is an increase of σ while above 523 K — reduction of conductivity and a rise in the activation energy of electrotransport.

An increase in conductivity after irradiation is typical almost for all the temperatures in LiF II crystals. Besides, two segments appear on the curve lg $\sigma(1/T)$ with a deviation from linear dependence which can be connected with complicated processes of aggregation of the radiation defects (stimulated by the presence of oxygen) during heating of the irradiated specimens.

4. Discussion

In the discussion of experimental results it is useful to give some interpretation of the following remarkable phenomena:

1) The nature of the maxima on the dependencees $\tau_I(T)$
2) The limiting mechanism of the deformation recovery
3) Specifics of the interaction of radiation defects with impurity centres in oxygen containing LiF.

The appearance of maxima on the temperature dependences of yield point (in LiF as well) was observed by many authors, and their connection with the formation of metastable phases is believed to be proved (Sarközi, Predvoditelev): the change of the shape of the maxima as well as the corresponding temperature under the influence of doping and γ-irradiation is a result of interaction of introduced impurities and radiation defects with impurity centres. This interaction causes a change in the composition and (or) structure of the impurity formations and the temperature interval of their stability. Comparing the experimental curves $\tau_I(T)$ and lg $\sigma(1/T)$ with published data (Buravleva et al.; Soifer; Willey, Newkirk; Reppich) it is possible to judge about the nature of impurity centres responsible for peaks of $\tau_I(T)$ and $\tau_{III}(T)$ in nonirradiated LiF I at 523 K and 673 K. According to lg $\sigma(1/T)$

(Fig. 5) decomposition of dipoles Me^{2+}-vacancy is terminated at 523 K, and according to Buravleva et al. at the same temperature in LiF(Mg) there is a transition of metastable phase to MgF_2 precipitates. Thus, the first peak on $\tau_I(T)$ can be connected with the formation of a stable MgF_2 phase. The peak at 673 K seems to correspond to the formation of Suzuki phase revealed in LiF(Mg) at this temperature and identified as $6\,LiF \cdot MgF_2$ (Soifer; Lilley, Newkirk; Reppich).

As for the origin of maxima of $\tau_I(T)$ graphs for LiF II, nothing definite can be said. One can only state that the corresponding hardening centres contain both cationic and anionic impurities combined with intrinsic point defects. At the temperature of the minimum on $\tau_I(T)$ the impurity centres, inhibiting plastic processes, are complexes of type $Me^{2+}O^{2-}$. Such a conclusion is evident from conductivity data: at temperatures of a minimum on the curve $\tau_I(T)$ there are excessive free vacancy pairs $V_c^-V_a^+$.

In our work the attention is paid to the change with temperature of not only yield point but of the stress, corresponding to the beginning of the deformation recovery, τ_{III}. In Figure 4 athe common tendency of reduction of τ_{III} at heating of LiF specimens is evident. Assuming that τ_{III} reduces along some curve on which two maxima at 523 K and 673 K are overlapped, it appears that the dependence $\lg \tau_{III}(1/T)$ is a straight line which can be described by equation

$$\tau_{III} = B \exp(E_\tau/kT)$$

where B is a constant, $E_\tau = 0.78$ eV — activation energy of the deformation recovery process.

It should be noted that the value $E_\tau = 0.78$ eV coincides with the migration energy of free cationic vacancies in LiF (Vora et al.; Bauer et al.), and the energy of reorientation of the dipoles $Mg^{2+}V_c^-$ (Matzke; Süplitz, Teltow). Thus, it is possible to conclude that the processes of exponential increasing of σ and lowering of τ_{III} in LiF I with increase in temperature, having indentical activation energies, are due to the same reason: increase in concentration of free cationic vacancies as a result of decomposition of $Me^{2+}V_c^-$ dipoles.

But the easier deformation recovery of irradiated LiF II compare to that of LiF I in wide temperature interval 400—600 K when according to lowes conductivity much less concentration of free cationic vacancies is present and must be rised the content of anionic vacancies due to oxygen, means that in the deformation recovery participate the anionic vacancies too.

The change of the mechanical and electrical properties of LiF I and LiF II crystals under the influence of γ-irradiation clearly demonstrates the interaction of radiation defects with impurity centres (cationic and anionic). It is evidenced by the following facts:

1) Disappearance of impurity softening at room temperature in LiF II
2) Change of jerky flow in LiF II caused by oxygen
3) Change of the limiting deformation towards reduction (LiF I) and increase (LiF II)
4) Complication of all temperature dependences and displacement of the stability temperature intervals of different impurity centres in LiF I and LiF II
5) Change of the level of the extrinsic conductivity in both crystals, appearance of non-linear segments in LiF II and increase of the activation energy of the formation of complexes $Me^{2+}V^-$ in LiF I.

The removal of impurity softening in LiF II after irradiation together with increase of ductility and reducing of jumps on stress strain curves and the displacement of the interval of jerky flow to lower temperatures — all these facts indicate that impurity complexes after the irradiation become smaller in dimension and bigger in number.

5. Conclusion

The complex study of the influence on mechanical and electrical properties of LiF crystals of impurities, γ-irradiation and testing temperature revealed a close interaction of all the three factors: under the influence of irradiation and temperature change the reconstruction of impurity centres takes place. Due to the interaction of radiation defects with impurities there is a change in impurity centre structure and in the role of impurities in the change of mechanical properties.

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