between the initial dipole concentration and the concentration of divalent ions indicated that there are very few inactive dipoles following the quenching from 400°C.

Iida, Y.: Is there any possibility that dipoles dissociate into single defects instead of clustering and that you are observing the effects? Secondly, this effect is essentially related to aging. Dislocations may play a very important role.

Dryden, J. S.: If the decay of dipole concentration was due to the dissociation of the dipoles, then the dc conductivity would increase because of an increase in vacancy concentration. This does not happen.

At one stage of the investigation we thought that the step in the decay curves may occur because dipoles were trapped near dislocations. An etch pit count revealed that the density of dislocations was too low by several orders of magnitude. Also the variation of dislocation density between different crystals was inconsistent with the idea that dislocations have any part in the aggregation.

Nowick, A. S.: Can you see any theoretical reason why dimers should be unstable?

Dryden, J. S.: No, other than the fact that if two dipoles are arranged so as to form a square there is a region of the crystal where some ions have a large fraction of their nearest neighbors as either defects or impurity ions.

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Study of the Lattice Defects in Normal and Neutron Irradiated Lithium Fluoride by Dielectric Relaxation Measurements

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Carefully annealed LiF crystals do not show any dielectric relaxation phenomena between 0°C and 100°C for frequencies between 10^2 and 10^5 c/s. After heating and quenching, divalent impurities associated with Li vacancies give a Debye domain of losses.

The effects on the dielectric properties of neutron irradiation at the reactor temperature is a complete inhibition of divalent impurities and creation of dipolar defects revealed by two domains of losses; the mobile part of the dipoles giving one of these domains are Li vacancies. The point defects created by low temperature irradiation are essentially different.

1. Non-Irradiated Samples

Carefully annealed LiF crystals do not show any dielectric relaxation phenomena between 0°C and 100°C for frequencies between 100 and 10^5 c/s. However the content of divalent impurities (mainly magnesium) is of the order of 10^{-4} as given by optical spectrometry. Were those impurities normally distributed in the lattice, in substitution, they would be accompanied by lithium ion vacancies for charge compensation and there would therefore be dipolar complexes Mg^{++} $\boxed{Li^+}$ which would give rise to a measurable dielectric relaxation effect such as has been observed by Dryden and Rao[1].

It must therefore be concluded that in those well annealed crystals the divalent impurities are inhibited and that no dipolar complexes of the type Mg^{++} $\boxed{Li^+}$ take place.

To remove this inhibition it is sufficient

to heat the crystals at a temperature higher than 150°C and to quench them rapidly. After this treatment there appears a very nice dielectric relaxation domain (we will call it LF_1) of which the Cole and Cole diagram is very nearly circular and fits well with that observed by Dryden and Rao. The activation energy of this domain, equal to 0.65 eV, is the same as the activation energy for the migration of $|\overline{Li^+}|$ vacancies deduced from electric conductivity measurements[2].

The maximum of the dissipation factor of the LF_1 domain is the larger, the higher the temperature from which the crystal was quenched. However, this dissipation factor reaches a saturation value for samples having been heated at 400°C. It corresponds to a divalent impurity content of 5.10^{-5}.

An anneal of these samples, followed by a very slow cooling down makes the relaxation effect disappear anew: the divalent impurities are therefore inhibited again because of the anneal[3].

2. Samples Irradiated at the Reactor Temperature

LiF lamellae which have been *irradiated to neutrons* (at the reactor temperature) at fluxes superior to 10^{17} nvt/cm^2 present two dielectric dispersion domains. One of these domains (we will call it LF_2) coincides with the LF_1 domain observed for quenched non-irradiated crystals; it therefore corresponds to the relaxation of dipoles in which the *mobile* part is again a $|\overline{Li^+}|$ vacancy. It is most likely that these dipoles, created by irradiation are associations of two vacancies $|\overline{F^-}|$ $|\overline{Li^+}|$. Indeed, the LF_2 losses appear in very pure crystals in which it was impossible to obtain LF_1 losses after quenching without irradiation. Thus, Mg $|\overline{Li^+}|$ dipoles cannot account for the explanation of LF_2 domain.

The other domain, called HF, which is observed at higher frequencies, has an activation energy of 0.4 eV[4].

We have followed the evolution of the irradiated samples during a thermal treatment. They undergo successive heatings for half an hour at temperatures varying by steps between 120°C and 500°C. Each time the samples are quenched and studied at 50°C.

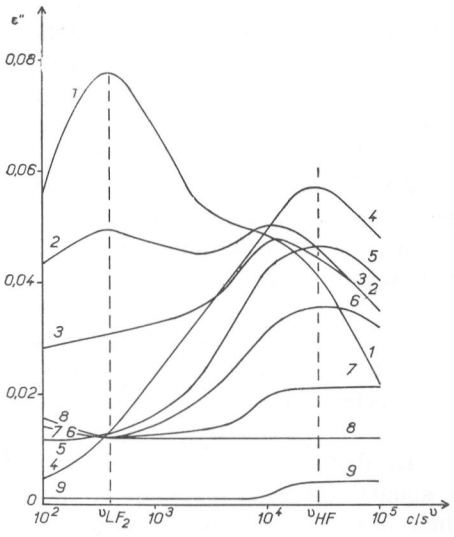

Fig. 1. Variations of the loss factor ε'' *versus* frequency. Temperature of the dielectric measurements: 50°C. Crystal has been neutron irradiated at the reactor temperature. Irradiation dose: 6.10^{17} nvt. The curves show the evolution of the losses after successive heat treatments.

Curve 1: no heat treatment, crystal as-received after irradiation.

Curves 2 to 9: heating of the crystal during 30 min followed by quenching.

Temperature of heating °C	130°	140°	160°	180°	200°	240°	280°	350° and 420°
No. of curve	2	3	4	5	6	7	8	9

After heating between 120°C and 180°C the losses of the LF_2 domain decrease progressively while these of the HF domain increase (fig. 1). After heating at 180°C, the LF_2 domain disappears completely and the losses of the HF domain are highest. A heating at temperatures between 180°C and 300°C leads to a progressive decrease of this HF domain, until it completely disappears.

Then, after a heating at 300°C followed by quenching, the irradiated samples do not present losses any more, even when the same thermal treatment applied to an identical but not irradiated crystal creates the LF_1 domain.

It is only after reaching total recovery of the sample, with bleaching, by a heating at 500°C that the losses of the LF_1 domain may reappear by quenching.

To sum up, the effects on the dielectric properties of neutron irradiation at the reactor temperature are (i) complete inhibition of divalent impurities, removed only by heating at 500°C, (ii) creation of dipolar defects revealed by two domains of losses, LF_2 and HF, the first one being removed by heating at 180°C, the second one at 300°C. The mobile part of the dipoles at the origin of the LF_2 domain is certainly a $\boxed{Li^+}$ vacancy.

3. Samples Irradiated at Low Temperature

The dielectric behaviour of samples irradiated at low temperature in a neutron reactor is different from that of samples irradiated at the reactor temperature. The samples irradiated at liquid nitrogen temperature do not present appreciable dielectric losses in the frequency range 10^2—10^5 c/s. Under low temperature irradiation none of the two relaxation domains LF_2 and HF observed in samples irradiated at the reactor temperature appear. The point defects created by low temperature irradiation are therefore essentially different from those resulting from irradiation at the reactor temperature. In low temperature irradiated samples, simple association of positive and negative vacancies does not exist any more. Similar conclusions can be drawn from electric conductivity measurements[5]. The proposed interpretation is as follows: at liquid nitrogen temperature the atomic defects (vacancies) are not very mobile. During low temperature irradiation they can therefore be trapped by electronic defects before they may be linked together or to divalent impurities.

Furthermore a heat treatment between 150°C and 400°C followed by rapid quenching does not make the LF_1 domain appear in these low temperature irradiated samples. Here also, as for the reactor temperature irradiated samples, the divalent impurities are inhibited and do not enter in Mg $\boxed{Li^+}$ dipoles until the total recovery by heating at 500°C.

Other experiments have been done or are being done on samples irradiated with gamma rays, samples irradiated and then optically bleached, etc···

The study of the dielectric behaviour of crystals adds therefore an interesting complement to the results of electric conductivity or optical absorption measurements for the determination of the nature and the behaviour of point defects in crystals.

References

1 J. S. Dryden and N. Rao: J. Chem. Phys. **25** (1956) 222.
2 P. Bergé: Bull. Soc. Fr. Min. Crist. **83** (1960) 57.
3 H. Curien and C. Petitjean: Comptes-Rendus Paris **253** (1961) 254.
4 H. Curien and J. Fructus-Ricquebourg: Comptes-Rendus Paris **253** (1961) 850.
5 P. Perio: *Proc. Int. Conf. Cryst. Latt. Def. (1962)*: J. Phys. Soc. Japan **18** Suppl. III (1963) 363.

DISCUSSION

Nowick, A. S.: You refer to the "inhibition" of the Mg. Is not the effect one of precipitation of the magnesium, and has the kinetics of the precipitation of Mg^{++} in LiF been studied?

Curien, H.: From experimental data, one can only conclude that after annealing (non-irradiated crystals) or irradiation, the magnesium does not belong any more to dipoles. We are currently investigating the kinetics of this "inhibition".