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LETTER TO THE EDITOR

Formation of radiation defects in KH_2PO_4: temperature dependence of the dose-rate effect

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Abstract. The 'dose-rate effect' has been studied in potassium dihydrogen phosphate (KDP) single crystals as a realisation of the peculiar mechanism of radiation defect formation in soft-mode crystals. The temperature dependence of the effect, calculated analytically on the basis of model concepts, is in agreement with that obtained experimentally. The possibility of the occurrence of a similar dose-rate effect during irradiation of highly correlated systems including chalcogenide glasses, charge-ordered systems and Mott's systems has been discussed.

The 'dose-rate effect' in potassium dihydrogen phosphate (KDP), a widely used non-linear optical material, was first observed in our earlier work [1]. The effect consists in the fact that for some constant absorbed dose of ionising radiation the radiation damage to the crystal is greater the lower the dose rate. Irradiation was performed at room temperature over the dose range 1.0×10^3–2.0×10^5 Gy and the dose rate range 0.15–13 Gy s^{-1}. Radiation damage was recorded spectrophotometrically according to radiation-induced optical absorption (figure 1). As is already known [2, 3], the UV absorption in KDP is due to the colour centres, which are proton vacancies associated with a polyvalent cation impurity (usually Fe^{3+}). The appearance of such colour centres under irradiation may be related to the change in the charge state of the impurity cation due to electron or hole trapping.

The dose rate effect has been described theoretically using the model of dispersed admixed centres placed in a soft-mode crystalline matrix with a strong electron–phonon interaction [4]. Summarising the results of the paper [4], we can formulate two conditions under which a similar dose-rate effect (by which we mean the effect due not to the recombination of defects, but to that of excitations generating defects) can be observed in the irradiated system. These are:

(i) The decay of some electron excitations is one mechanism by which radiation defects are formed in the system.

(ii) There exists an effective interaction between the excitations leading to their lifetime being highly dependent on their concentration.

The type of the effective interaction is determined by the intrinsic properties of the irradiated material. In soft-mode crystals, particularly in KDP, it is of the electron–phonon type. It is clear that the occurrence of condition (ii) unambiguously

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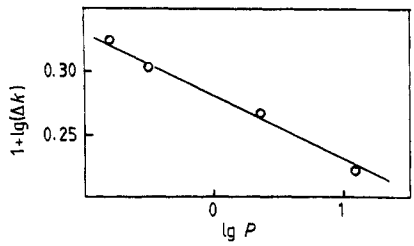

Figure 1. The dependence of the absorption coefficient Δk (cm^{-1}) in the peak of the radiation-induced optical absorption band (λ = 270 nm) on the dose rate P ($Gy\,s^{-1}$) for KH_2PO_4 (KDP) single crystals irradiated at T_{room} up to the dose 1.0×10^3 Gy (according to data reported in [1]).

determines the direction of the effect, namely that increasing the dose rate at a constant absorbed dose may only result in a decrease in the concentration of defects formed according to condition (i).

Proceeding from the model concepts, an analytical expression for the coefficient α_2 [4] that determines the magnitude of the dose rate effect, was obtained:

$$\alpha_2 = C \sum_k \frac{\tau_k}{\omega_k^4 \varepsilon^2(k)} \tag{1}$$

where C is the coefficient dependent in particular on the constants of the electron–phonon interaction, τ_k and $\varepsilon(k)$ are respectively the lifetime and energy of the excitation of the electron sub-system and ω_k is the dispersion of the soft-phonon mode. From equation (1) and the known temperature dependences for the ω_k (see, for example [5]) and τ_k [6], it follows that over a wide temperature range above the Curie point, T_C

$$\alpha_2 \simeq (T - T_C)^{-1.5}.$$

Below the Curie point the low-lying phonon modes are absent; therefore the dose-rate effect cannot be observed at such temperatures. The temperature dependence of the dose-rate effect must be determined by the temperature dependence of α_2, i.e. by the critical dependence of the form $(T - T_C)^{-a}$.

To test this statement the temperature dependence of the dose-rate effect was investigated. The experiments were performed on Z-cut KDP plates of thickness 0.5 cm. A high degree of uniformity of the samples was ensured by cutting them from some specific locations nominally in pure, high-quality single crystals grown by industrial technology. Irradiation was performed at 77, 143, 178, 195, 250 and 300 K using ^{60}Co γ-sources up to an absorbed dose of 4.0×10^3 Gy at two dose rates, 0.2 and 9.5 $Gy\,s^{-1}$. Optical absorption spectra were recorded before and after irradiation at room temperature using a Specord-40M spectrophotometer over the range of wavenumbers 52 000–11 000 cm^{-1}. The recorded radiation-induced optical absorption in the samples irradiated at $T < T_{room}$ and then warmed to T_{room} is stable and not annealed up to the crystal decomposition temperature (figure 2).

It was established that:

(i) In all the crystals investigated, irradiated at temperatures above $T_C = 122$ K the dose-rate effect occurs, i.e. at a constant absorbed dose the radiation-induced optical absorption is the greater the lower the dose rate.

(ii) In crystal, irradiated at $T = 77\,K < T_C$, the dose-rate effect was not observed.

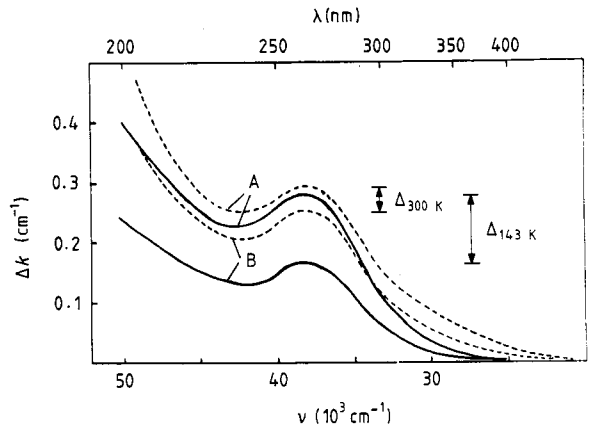

Figure 2. Optical absorption spectra recorded at T_{room} of KDP single crystals γ-irradiated up to a dose of 4.0×10^3 Gy. Full curves, irradiation at 143 K, broken curves, irradiation at 300 K. A, dose rate 0.2 Gy s^{-1}; B, dose rate 9.5 Gy s^{-1}.

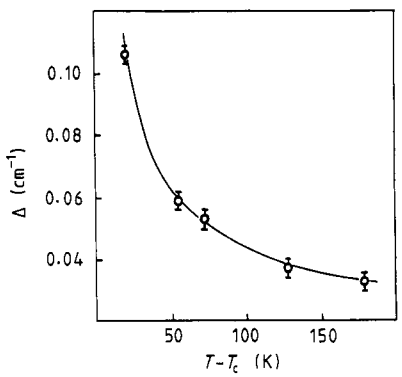

Figure 3. The dependence of Δ (see text) on $(T - T_C)$ for KDP crystals γ-irradiated up to a dose of 4.0×10^3 Gy.

To estimate the effect at the given irradiation temperature T the value

$$\Delta_T = \Delta k_{min} - \Delta k_{max}\ (cm^{-1})$$

was used, where Δk_{min}, Δk_{max} are the absorption coefficients in the peak of the radiation-induced optical absorption band at 380000 cm^{-1} for the samples irradiated at the minimum (0.2 Gy s^{-1}) and maximum (9.5 Gy s^{-1}) dose rates, respectively.

It can be shown that the change Δ with the change of the irradiation temperature characterises the temperature dependence of α_2. The dependence of Δ on $(T - T_C)$ is shown in figure 3. The experiments demonstrated that the Δ_T depend to a large degree on the pre-history of the sample and on the amount of uncontrolled impurity. Nevertheless, the experimental dependence obtained is quite well described by the law $(T - T_C)^{-a}$ with $a = 0.56$. The difference of the power from the theoretically obtained value of 1.5 can be due to the one-mode approximation, critical effects and the fact that the excitation lifetime τ was evaluated in terms of perturbation theory. Thus, the experiment performed qualitatively confirms the predicted critical dependence of the effect on temperature.

In conclusion, it is to be noted that the class of compounds in which the necessary conditions for a similar dose-rate effect hold can be considerably enlarged due to highly correlated systems, for example, superconductors, magnetic systems and also systems with local electron pairs, namely, charge-ordered systems and chalcogenide glasses. The formation of electron pairs in such systems is due to the presence of an effective short-range attraction between the electrons located on one lattice site. At temperatures below some definite T, these sites (or centres) are either vacant or filled with a pair of electrons. The formation of one-electron defects in similar systems may occur as a result of the excitations arising from the decay of the electron pair on the vacant lattice site. The probability of the recombination of such excitations is determined by the probability of the coupling of single electrons. In dielectrics, the higher the electron concentration the greater this probability. The study of systems that are subject to the Mott transition at some definite temperature is also of great interest. At low temperatures such systems are known to possess a dielectric gap resulting from the Coulomb repulsion between electrons. The temperature rise makes the dielectric state unstable with respect to the excitation mode related to the electron excitation to the conductivity band. This excitation mode may be responsible for the formation of electron structure defects, for example, those representing anomalously charged (with respect to their ordinary charge state in the given matrix) ions of the polyvalent impurity. Again, the higher the impurity concentration, the greater the probability of the recombination of such excitations.

Thus, the quest for the dose-rate effect in the highly correlated systems above may considerably broaden the existing concept of the mechanisms of radiation damage in solids.

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