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Effect of the $V^- \leftrightarrow V^=\$ transformation on positron annihilation lifetime spectra in MgO

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1. Introduction. — Positron annihilation techniques have become increasingly popular for studying defects in solids [1-3]. Cation vacancies, produced by charge compensation in KCl : Ca$^{2+}$ have produced positron lifetime spectral effects [4-6] which are apparently insensitive to the degree of association between the vacancies and the Ca$^{2+}$ ions [3, 6], although our unpublished studies of MgO : $R^{2+}$ ($R = Al$, Cr, Fe) show spectra which are sensitive to heat-treatment. In principle a particularly simple exercise should be to study bleaching and recoloring of (isolated) $V^-$ centers in MgO by the lifetime technique, as in a previous study of F centers in KCl [7]. Isolated cation vacancies in MgO are designated $[8]$ as $V^-$ and $V^=$ centers respectively when they are bare and when each traps a hole after suitable irradiation.

2. Experimental. — Positron lifetime spectra were measured as described elsewhere [9]. Samples were pairs of single crystal blocks, $\sim 10 \times 10 \times 2$ mm in size, and the $e^-$ penetration into MgO would have been $\sim 70 \mu$m [2]. Spectra were accumulated over 24 hr and the peak number of counts in a spectrum was $\sim 3 \times 10^8$.

To maximize the $V^-$ concentration, crystals with $V_{OH}^-$ concentrations as high as possible were irradiated with fast electrons [11]. Deuterated ORNL MgO was used as IR measurements showed the $V_{OD}^-$ concentration was greater than the $V_{OH}^-$ concentration in other material at our disposal. A somewhat cloudy sample pair was used since $H(D)$ concentrates in the cloudy regions of arc-melted hydrated (deuterated) MgO crystals [11] and it was quenched from $1000 \, ^\circ C$ to maximize the $V_{OH}^-$ concentration. The $V_{OH}^-$ concentration was $\sim 25 \%$ that of the $V_{OD}^-$ centers.

After measuring the positron lifetime spectrum, the sample was irradiated (Operation I) with $\sim 10^{18} \, cm^{-2}$ of 2 MeV electrons. IR measurements made 6 days later showed $\sim 70 \%$ of the $V_{OD}(V_{OH})$ centers had been converted to $V^-$ centers. From the intensity of the $\sim 18 \, 500 \, cm^{-1}$ optical absorption band, the $V^-$ concentration at this stage was found to be $\sim 1 \times 10^{18} \, cm^{-3}$ or $20 \, ppm$ ($\pm 25 \%$) [11]. $V_{OD}(V_{OH})$ centers would have reverted to $V_{OD}^-(V_{OH}^-)$ centers, most of the $V_{AI}$ centers would have decayed, and most of the $V_{OH}$ centers should have formed $V^-$ centers [10-12]. The electron-induced optical absorption band near $40 \, 000 \, cm^{-1}$ showed the concentration of F-type centers to be $\sim 1 \times 10^{18} \, cm^{-3}$ or $20 \, ppm$ ($\pm 25 \%$) [13]. Since $\sim 10^{18} \, F$ centers $cm^{-3}$ were necessary to produce well-defined positron lifetime effects in KCl [7], the F-type centers in MgO were expected to have little effect, especially as the bleaching and recoloring operations subsequently applied to the isolated cation vacancies should not have affected the atomic or electronic structures of the F-type centers [10].

Further positron lifetime spectra were measured after:

II. 20 hr optical bleaching in the V band which removed $\sim 60 \%$ of the $V^-$ centers,

III. 2 MR of $\gamma$-radiation which recolored the $V^-$ centers,

IV. 3 hr of thermal bleaching at $175 \, ^\circ C$ which produced $100 \%$ color discharge [1 hr at $175 \, ^\circ C$ was insufficient. After 3 hr bleaching, IR measurements showed $\sim 50 \%$ of the isolated cation vacancies had reverted to $V_{OD}^-$. $V_{OH}^-$ centers].
V. 2 MR of \( \gamma \)-radiation to recolor the remaining \( V^+ \) centers, and

VI. requenching from 1000 °C to restore the sample to its condition before electron irradiation.

3. Results. — Figure 1 shows a normalized positron lifetime spectrum (after background subtraction) for the purest available MgO. The spectrum can be decomposed into three exponentials, characterized by the intensities and lifetimes as follows:

\[
I_2 = 19 \pm 2 \%, \quad I_3 = 1.2 \pm 0.1 \%,
\]

\[
\tau_1 = 0.18 \pm 0.01 \text{ ns}, \quad \tau_2 = 0.44 \pm 0.02 \text{ ns},
\]

\[
\tau_3 = 1.62 \pm 0.10 \text{ ns}.
\]

\( \tau_1 \) agreed with the value given for powdered MgO [14]. The cloudy, but not the optically-clear, deuterated MgO gave an enhancement of the longer-lived intensity components in the lifetime spectrum relative to pure MgO (Fig. 2a). Electron-irradiation of the cloudy sample removed the enhancement (Fig. 2b) and reduced the longer-lived components below the corresponding values for pure MgO.

Optical bleaching (Operation II, see above) produced a further reduction of the longer-lived components (Fig. 2c) and this reduction was largely removed by recoloring (Operation III). As expected, thermal bleaching (Operation IV) produced a larger reduction of the longer-lived components than the less-efficient optical bleach, but recoloring (Operation V) did not completely remove this effect (Fig. 2c), presumably because of \( D^+(H^+) \) migration in the thermal bleach. Requenching (Operation VI) essentially reproduced the lifetime spectrum obtained in the quenched sample before electron irradiation.

Any changes in the lifetime spectra due to changes of charge state of \( V_{\text{OD}}(V_{\text{OH}}) \) centers were negligible because enough time at room temperature was allowed to elapse after \( \gamma \)-irradiation for \( V_{\text{OD}}(V_{\text{OH}}) \) centers to decay before the lifetime data were taken. The relative concentration of \( V_{\text{AI}} \) centers was small.

The formal statistical errors in the number of annihilation events in the time channels appropriate to the difference spectra were insignificant but other systematic errors such as drifts in the resolution function and in the time base were present. Approximate statistical errors are shown in figure 2d.

At this stage, we are unable to quantify the spectral changes in terms of changes in the three-lifetime data fits; hence the difference spectra mode of presentation. [Note all spectra were normalized to constant intensity at \( t = 0 \).]

4. Discussion. — The principal result is that the longer-lived components of the lifetime spectrum were enhanced when the \( V^- \) centers were formed by hole trapping and reduced when \( V^+ \) centers were produced by bleaching. The reverse effect would be expected if the longer-lived components derived from free positron annihilation in (electron-deficient) cation vacancies because the coulomb attraction between a \( V^- \) and the \( e^+ \) would be greater than that for a \( V^- \) and the \( e^+ \). Moreover, when a cation vacancy traps a hole and becomes equivalently less negatively charged, the coulomb repulsion of its anionic nearest neighbors will fall and the relaxation will increase.
the size of the vacancy, again leading to a result qualitatively opposite to that observed. This argument should hold irrespective of the distribution of the hole charge in the vacancy and on the anionic neighbors. The only obvious possibility to explain the experimental observations is that a complex radical involving $O^-$ and the $e^+$ forms but no other information is available.

That the cloudy, but not the clear, deuterated MgO showed an enhancement of the longer-lived spectral components relative to pure MgO, would seem unrelated to the $V_{OD}$, $V_{OH}$ concentration, as this concentration in the clear sample was $\sim 80 \%$ that in the cloudy sample. Also, neither crystal showed significant spectral changes when the $V_{OD}$, $V_{OH}$ concentrations was reduced from $\sim 30$ to $\sim 15$ ppm by slow-cooling from 1000 °C instead of quenching. Thus the enhancement in the cloudy sample is probably due to defect sites and gases in the voids producing the cloudiness. The reduction of this enhancement on electron-irradiation presumably reflects modification of the defect sites and/or the gas distribution.

Finally, it was not clear, in the absence of a control electron-irradiation experiment on clear deuterated (hydrogenated) MgO, whether $V^-$ centers produced any modification of the positron lifetime spectrum. However a possible interpretation of our unpublished results on MgO : $R^{3+}$ is that relatively isolated cation vacancies do enhance the longer-lived spectral components. Clearly more experimental and theoretical work is required to understand positron annihilation in $V^-$ and $V^+$ centers in MgO.

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**DISCUSSION**

*Question.* — A. E. Hughes.

Do you have any explanation for the fact that $V^-$ centers seem to be better positron traps than $V^+$ centers?

*Reply.* — W. C. Mallard.

As yet, we do not have models adequate to explain these observations.

**References**