Short Notes

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Paramagnetic Thermoluminescent Centers in $CaWO_4$ [1)]

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The purpose of this note is to point out the possible relations of the thermoluminescent (TL) EPR centers studied in our laboratory (1, 2) and those reported recently by Born, Grasser, and Scharmann (3).

Our measurements were made on nominally pure single crystals (2x2x4 mm^3) of $CaWO_4$, obtained from the Harry Diamond Laboratories and the Isomet Corporation. The samples were γ -irradiated in the Phoenix Memorial Laboratory cobalt-60 source at 78 $^{\circ}$K, with an estimated dosage of about 300 krad, or about $10^{15\pm1}$ γ -quanta.

The samples were initially transparent but became dark after irradiation; however, the discoloration could be annealed out by heating to 700 $^{\circ}$K for about 40 h.

The glow curves of all nominally pure samples showed three distinct peaks at 155, 225, and 290 $^{\circ}$K respectively. These peaks can be removed separately by heating the sample to about 190, 250, and 350 $^{\circ}$K. Fig. 1 shows the effect of successive cyclic heating upon the EPR spectra. The EPR spectra were taken at 78 $^{\circ}$K.

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4) "Nominally pure $CaWO_4$" refers to $CaWO_4$ as grown with no intended impurities.

See Short Note by H. A. KOEHLER et al.

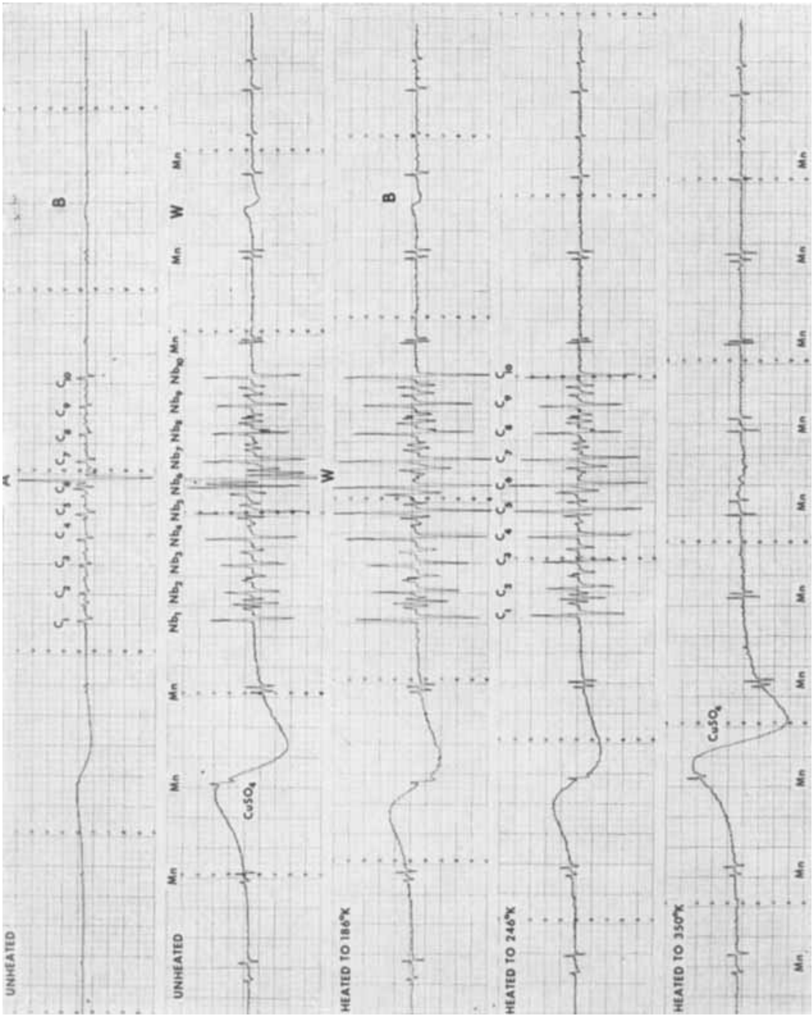

Fig. 1. EPR spectra of γ-irradiated (300 krad) pure $CaWO_4$ at 78 °K after differential thermal annealing. ***H*** parallel to [001] axis

See Short Note by H. A. KOEHLER et al.

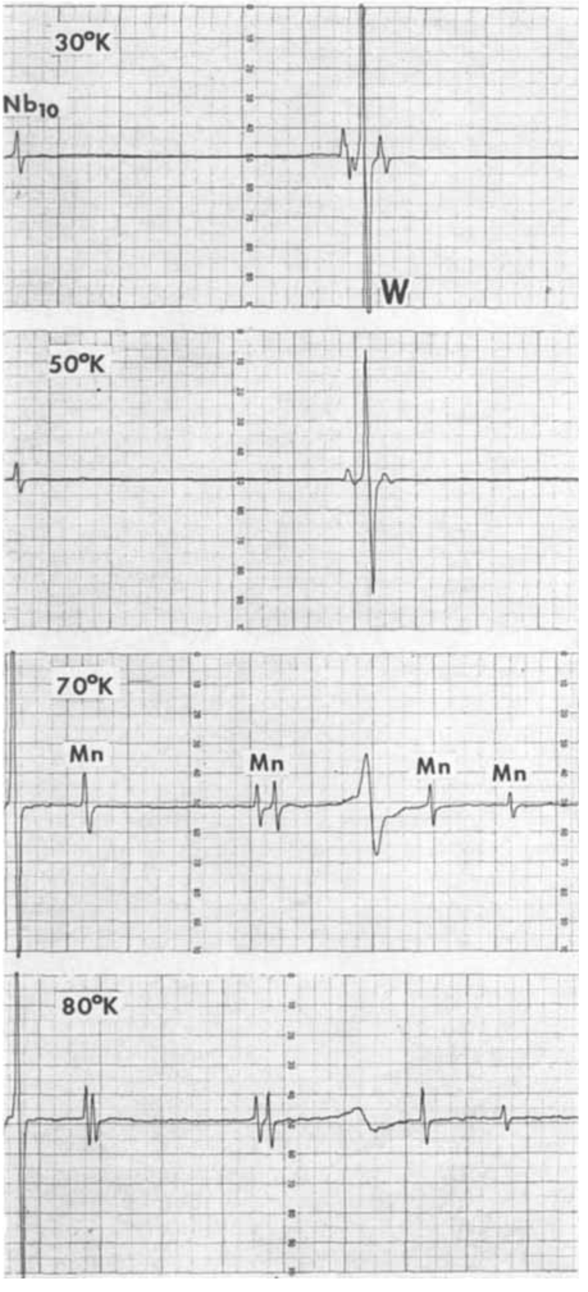

Fig. 2. Temperature dependence of group B spectrum of γ-irradiated (300 krad) pure $CaWO_4$. $\boldsymbol{H}$ parallel to [001] axis

The top trace was obtained immediately after γ -irradiation. The weak lines are due to Mn^{+2}, the group of ten lines (C_1 to C_{10}) to Nb^{+4}, and the A and B lines to W^{+5}, as will be discussed presently. The second trace was obtained under higher EPR spectrometer gain. The third trace was obtained at 78 $^{\circ}$K after warming the sample to 186 $^{\circ}$K to remove the first TL peak. Note that line A has disappeared. Similar procedures were repeated to identify the second (225 $^{\circ}$K) and third (290 $^{\circ}$K) TL peaks with group B and C EPR lines. As mentioned earlier (1) paramagnetic Nb^{+4} ions are responsible for the C lines.

Our suggestion is that the A line is the TL EPR center reported by Born et al. The g-value for this line varies from 2.009 along [001] to 2.019 along [110], and is to be compared to the values 2.009 and 2.0173 reported by Zeldes and Livingston (4).

The high field B line is also due to tungsten. This identification was made by gradually warming the sample from 4.2 to 80 $^{\circ}$K. Fig. 2 shows that at low temperature, say 30 $^{\circ}$K, the B line is seen to be a triplet, with relative intensities expected for tungsten. As the sample temperature is raised, the line broadens into a single line. This single broad line is possibly to be identified with the low g-value line reported by Born et al. According to our measurements, the g-values are 1.843 along [001] and 1.605 along [110]. Zeldes and Livingston reported 1.846 and 1.604 respectively.

We have tentatively assigned the B line to WO_3^- associated with a Ca vacancy; i.e. a paramagnetic tungsten associated with an oxygen-calcium vacancy pair. The center for the A line appears to be more complex. Observations indicate that at low irradiation dosages the C line intensity increases as the A line is annealed out. This suggests that the paramagnetic tungsten is in some way coupled to one or more niobiums.

The single broad glow curve seen by Born et al. compared to ours consisting of several peaks, may stem from the difference in impurity content. It is possible that the impurity content of their sample is higher than ours. According to our observation the glow curve is markedly altered by impurities. For example, we find that the A line is absent in all rare-earth doped samples.

Further details will be published elsewhere. We wish to thank R. T. Farrar of the Harry Diamond Laboratories for the $CaWO_4$ crystals and also S. Irizarry-Milan for providing the results shown in Fig. 2 and many helpful discussions.

References

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