

dal at high  $n$  (a characteristic of the spin-wave equation in a weakly inhomogeneous film) and this together with the surface boundary conditions<sup>9</sup> gives quadratic mode spacing. The intensities in this case are functions of the inhomogeneity. Quadratic spacing of high-order modes is almost independent of the model chosen for the film and cannot be presented as evidence for a particular model.

Thus the data presented in Figs. 1 and 2 of Ref. 1 do not confirm Kittel's model nor do they differ substantially from data presented previously.<sup>6-8</sup> The data are suggestive of a weakly inhomogeneous film, the inhomogeneity being asymmetric about the center of the film. In order to arrive at a model of spin-wave resonance in a film, it is necessary to study the lower order modes and to do additional measurements such as the determination of the spectrum as a function of frequency and as a function of the angle between the film and the static magnetic field.<sup>7,10</sup>

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<sup>9</sup>If the surface anisotropy  $K_S$  is very strong, one will have complete pinning. If it is not very strong, the Kittel-Rado-Weertman condition for nonpinning,  $2Ak \gg K_S^{(2)}$  [G. T. Rado and J. R. Weertman, J. Phys. Chem. Solids 11, 315 (1959), where  $A$  is the exchange parameter, will eventually be satisfied as the spin-wave vector  $k$  increases. The value of  $K_S$  has been calculated [G. T. Rado and J. R. Weertman, J. Phys. Chem Solids 11, 315 (1959)] and determined experimentally [B. Waksman, O. Massenet, P. Escudier, and C. F. Kooi, to be published] to be  $K_S \leq 0.1$  erg/cm<sup>2</sup> for Permalloy. Thus with  $A = 10^{-6}$  erg/cm the foregoing inequality is satisfied for the higher order modes of Ref. 1.

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## IDENTIFICATION OF DEFECT SITES IN $\text{CaWO}_4$ FROM THE CORRELATION OF ESR AND THERMOLUMINESCENCE MEASUREMENTS

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We wish to report the first positive identification of defect sites in nominally pure  $\text{CaWO}_4$  from careful correlation of ESR and thermoluminescence measurements. Since thermoluminescence results from the release of a trapped electron into the conduction band and subsequent return to the valence band, it is possible to observe by ESR this trapped electron if it has an unpaired spin. The paramagnetic ions  $\text{W}^{5+}$  and  $\text{Nb}^{4+}$  have been identified as the location of such trapped electrons.

The thermoluminescence curves of  $\text{CaWO}_4$  after  $\gamma$  irradiation at 77°K revealed three prominent peaks at approximately 155, 225, and 290°K as shown in Fig. 1. Similar distinct thermoluminescence peaks were observed in differently doped  $\text{CaWO}_4$  samples obtained from various sources.<sup>1</sup> Analysis of these results<sup>2,3</sup> leads us to believe that the electron traps are basic to the host lattice. Although the trap

depth and frequency factor were calculated for each peak, the inherent limitation of the thermoluminescence method made any identification of the defect sites impossible.

The ESR spectrum of pure  $\text{CaWO}_4$  after  $\gamma$  irradiation at 77°K showed two sets of lines near  $g = 2$  prior to heating. One set had a strong central line with two lower intensity lines equally spaced on either side when the magnetic field was parallel with the  $c$  axis of the crystal. The lines split into two components in the  $a$ - $b$  plane and into four components when the magnetic field was in any other direction. By comparison with previous results,<sup>4</sup> these lines were attributed to the paramagnetic tungstate complex with an associated defect. The second set of lines consisted of ten lines approximately equal in intensity and spacing when the magnetic field was along the  $c$  axis. A similar spectrum has been observed and assigned<sup>5</sup> to the

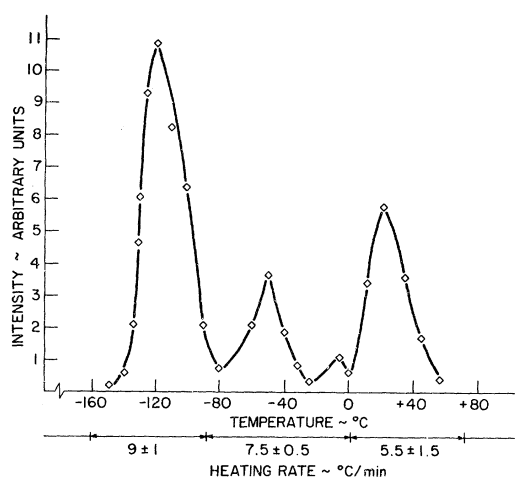


FIG. 1. Characteristic thermoluminescence curve of nominally pure  $\text{CaWO}_4$  after gamma irradiation of 300 krad at 77°K. Emission monitored at 4900 Å.

$\text{Nb}^{4+}$  ion in the tungsten site of  $\text{CaWO}_4$ . Hence we have concluded that the two sets of lines can be attributed to  $\text{W}^{5+}$  and  $\text{Nb}^{4+}$  located within the tungstate complex.

After the sample had been heated to approximately 195°K and recooled to 77°K, the  $\text{W}^{5+}$  lines were no longer observed. The elimination of the first thermoluminescence peak by a similar heating cycle has been verified independently. No further change in the ESR spectrum was detected after a similar heating cycle to 273°K. However, when the sample was heated to 315°K and recooled to 77°K, the  $\text{Nb}^{4+}$  spectrum had disappeared. Thermoluminescence measurements have shown that all of the thermoluminescence peaks can be removed by such cyclic heating. By maintaining the signal at

a fixed temperature, we eliminated any adverse temperature effects which may have altered the ESR spectra and the detection system.

We conclude that the first thermoluminescence peak in  $\text{CaWO}_4$  is due to the release of an electron trapped at a tungstate complex. Such a defect, characteristic of the lattice, is in accord with the conclusions reached from examination of the thermoluminescence data obtained from a wide selection of doped and undoped samples. The third thermoluminescence peak is attributed to  $\text{Nb}^{4+}$  in a tungsten site. The unexpected occurrence of niobium in all of the samples is not unduly surprising, since it is probable that there was a common supplier of the  $\text{CaWO}_4$  powder used as a source material for the single-crystal growth.

It is possible that a nonparamagnetic trapped electron gives rise to the second thermoluminescence peak. Investigations are presently in progress in an attempt to clarify this point, and to study further the role of impurities in the thermoluminescent behavior of  $\text{CaWO}_4$ .

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