EXCITATION, RELAXATION, AND CONTINUOUS MASER ACTION IN THE 2.613-MICRON TRANSITION OF $CaF_2:U^{3+}$†

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This Letter describes an investigation of the 2.613 μ fluorescence of trivalent uranium in CaF_2 ($CaF_2:U^{3+}$) and the operation of a continuous solid-state maser using this transition.

The optical properties of $CaF_2:U^{3+}$ were first investigated by Galkin and Feofilov,[1,2] who, in addition to obtaining the absorption spectrum, discovered a number of fluorescent lines between 2.1 and 2.6 microns. Sorokin and Stevenson[3,4] succeeded in obtaining pulsed optical maser action at 2.5 and 2.6 microns. Some maser experiments on this material between 77°K and 300°K were reported by Miles.[5]

The 2.613 μ emission was identified, by paramagnetic resonance, with U^{3+} ions in charge-compensated sites possessing a fourfold symmetry axis along the ⟨100⟩ directions.[6] The optical absorption spectrum of a crystal containing tetragonal sites in large predominance is shown in Fig. 1. In addition, investigation of some twenty $CaF_2:U^{3+}$ crystals showed the frequent existence of U^{3+} ions in sites of threefold symmetry and in

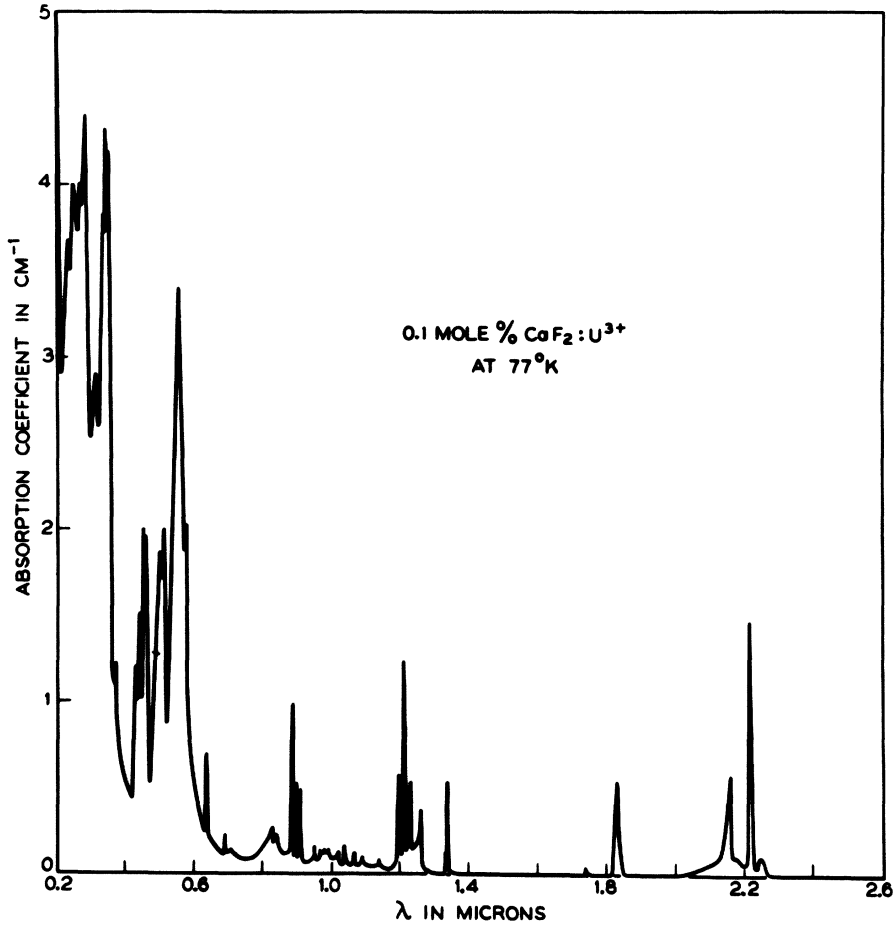

FIG. 1. The absorption of $CaF_2:U^{3+}$ as a function of wave-length.

sites lacking a symmetry axis.[7] Crystals containing significant fractions of ions in these lower symmetry sites have noticeably different optical absorption spectra, and characteristically have higher maser thresholds. The following discussion is pertinent to crystals containing greater than 95% tetragonal sites.

The useful excitation region of the 2.613 μ fluorescence was determined by placing Corning sharp-cutoff filters between a xenon flash lamp and the maser crystal. By this method it was found that the useful excitation is limited mainly to the 0.88 μ-0.92 μ region where there are three weak lines with oscillator strengths $f \approx 10^{-5}$ and widths $\Delta\nu \approx 15$ cm^{-1}. These lines correspond to transitions between the Stark split $^4I_{9/2}$ multiplet and the excited $^4I_{15/2}$ multiplet and are shown in Fig. 1. Elimination of all visible radiation increases the threshold by ≈15% and elimination of all radiation below 0.5 μ has only a negligible effect. Thus only a small part (≈15%) of the 2.613 μ fluorescence is due to absorption by the intense band ($f \approx 10^{-3}$) spanning the 0.5 μ-0.6 μ region.

The pertinent energy levels are shown in Fig. 2. The 2.613 μ emission is assigned to a transition between the lowest lying level of the $^4I_{11/2}$ group lying 4436 cm^{-1} above the ground state and a terminal level at 609 cm^{-1} belonging to $^4I_{9/2}$. The position of the terminal level has been deduced by subtracting 3827 cm^{-1} (2.613 μ) from 4436 cm^{-1}, the position of the metastable state. This assignment is somewhat tentative since it is based on absorption data at 300°K, 77°K, 20°K, and 2°K which revealed only five levels belonging to $^4I_{11/2}$. The expected number of levels for $J = \frac{11}{2}$ in a crystalline field of tetragonal symmetry is six (Kramers doublets). A contemplated emission experiment at a number of temperatures may clarify this point.

The lifetime of the metastable state at 4436 cm^{-1} was measured by monitoring the fluorescence decay following excitation by sharp light pulses. At 4.2°K, 20°K, and 77°K the lifetime is $\tau = 130 \pm 15$ μsec. At 90°K the lifetime decreases to 95 ± 15 μsec, while at 300°K the lifetime was shorter than 15 μsec, which was the resolution time of the experiment. These results are at variance with the reported[4] findings of Sorokin and Stevenson, who report a major reduction of τ between 4.2°K and 77°K.

The constant value of τ and the observed exponential nature of the fluorescence decay up to 77°K suggest that the lifetime up to 77°K is radiative and that the cascading time from the absorption bands down to the metastable state is much shorter than the metastable band lifetime.

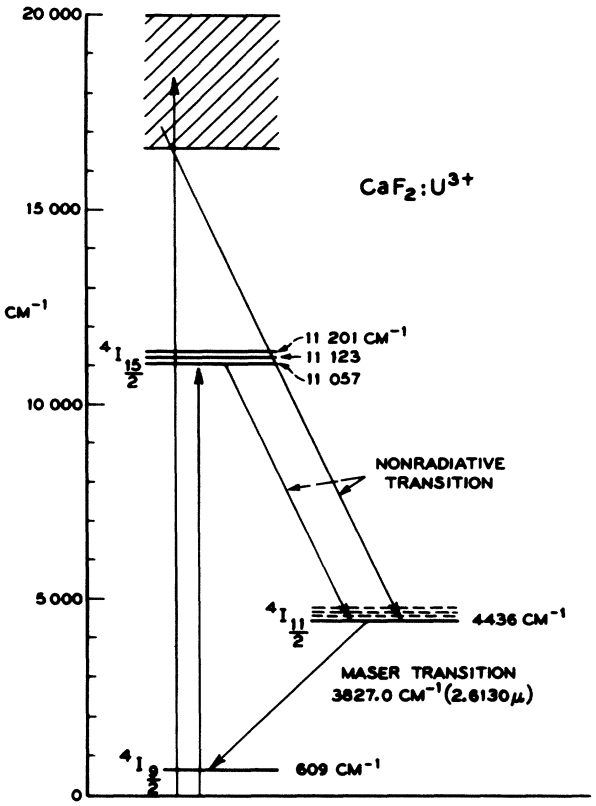

FIG. 2. The absorption-fluorescence cycle of the 2.613-micron transition in $CaF_2:U^{3+}$.

The threshold energy input to an FT-524 flash lamp surrounding the maser crystal was: 2.0 joules at 20°K, 3.78 joules at 77°K, 4.35 joules at 90°K, and ≈1200 joules at 300°K. The increase in threshold energy between 20°K and 77°K is due to the depopulation of the metastable state at the higher temperatures. This thermalization is significant, since there are a number of levels whose separation from the metastable state is smaller than 20 cm^{-1}. These low threshold values are typical of crystals with tetragonal sites only (fraction of tetragonal sites > 0.95).

The experimental arrangement used to obtain continuous maser action is illustrated by Fig. 3. The illumination was provided by a GE AH-6 Hg lamp placed along one focal axis of an elliptical cylinder. The $CaF_2:U^{3+}$ resonator was placed along the other axis. The focusing action of the elliptical cylinder yielded the necessary energy flux.

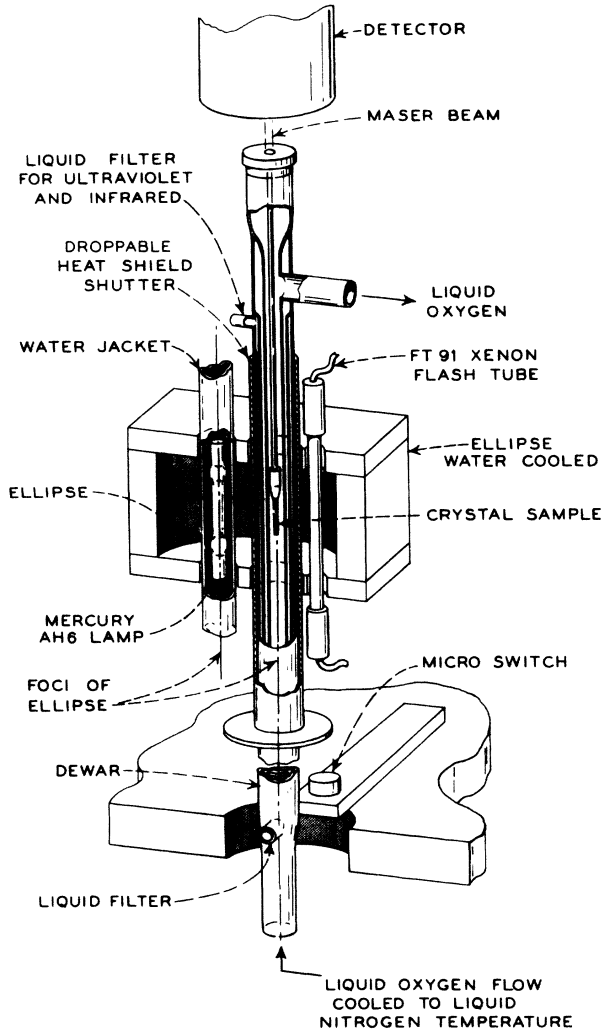

FIG. 3. Experimental setup for continuous maser operation.

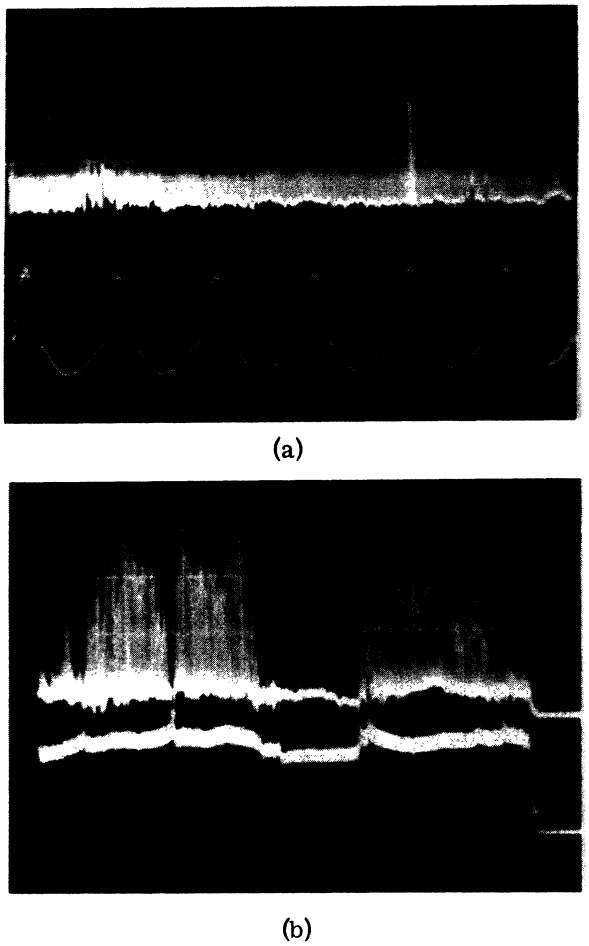

FIG. 4. (a) Upper trace: output from $CaF_2:U^{3+}$ maser (monitored by a PbSe detector) with ac power applied to lamp. Sweep rate 5 sec/division. Lower trace: a portion from the upper trace expanded by $\times 1000$. The bottom excursions correspond to fluorescence while the spikes are maser output. Sweep rate 5 msec/division. (b) Upper trace: maser output with dc power (2 kw) applied to the AH-6. Sweep rate 5 sec/division. Lower trace: light output from the AH-6. Sweep rate 5 sec/division.

The optical resonator was of the confocal type recently described by Boyd and Gordon.[8]

Cooling was provided by a continuous flow of liquid oxygen precooled to 77°K. The cooling mechanism is one of boiling heat transfer and thus takes advantage of the large heat of vaporization of liquid oxygen. Precooling was essential to eliminate bubbling which is detrimental to the heat contact between the crystal and the coolant. The cooling problem was further alleviated by circulating a liquid filter, consisting of a dilute solution of $K_2Cr_2O_7$, in the outer annular region of the double-flow Dewar, surrounding the crystal. This filters out the useless radiation at $\lambda < 0.5\ \mu$ which is otherwise readily absorbed by the crystal. The emitted $2.613\ \mu$ radiation was detected by a PbSe detector having a response time $\approx 5\ \mu$sec.

The experimental setup described above was also used recently[9] to achieve continuous maser action in $CaWO_4:Nd^{3+}$.

Figure 4(a) shows optical maser action with 1150 watts of 60-cps power applied to the lamp. Due to this ac excitation, the pump light is turned on 120 times per second. The upper trace at 5 sec/division shows the output of the PbSe detector monitoring the silvered face of the crystal, which was left slightly ($\approx 1\%$) transmissive. The lower trace

shows a portion of the upper one expanded by $\times 1000$ (sweep rate = 5 msec/division). The sharp spikes at the top of each excursion correspond to stimulated emission. The excursions themselves are due to the fluorescence and stray lamp light and have the same shape as the light output from the AH-6 lamp.

Figure 4(b) shows continuous maser action with dc power applied to the lamp. The upper trace shows the output of the PbSe detector, while the lower trace shows the dc light intensity as monitored by a phototube. Both traces are swept at 5 sec/division. Note that in the middle of the 50-sec sweep the lamp intensity was reduced by $\approx 20\%$ for 7 sec and the maser action during this period was observed to cease. At the end of the sweep the lamp is extinguished, showing the zero level for both traces. The violent fluctuations in the maser output envelope are due to the ac ripple in the dc supply. When threshold is barely exceeded, a small ripple in the pump intensity is a large variation in that part of the light intensity which is above threshold. Power levels observed thus far are around 10 microwatts. This may well be increased by switching to continuous xenon lamps, which have more energy around 0.9 μ than do mercury lamps.

The relaxation oscillations present in the pulsed operation of $CaF_2:U^{3+}$ maser[4] were observed to die out in a few milliseconds after the onset of maser action. Such also has been observed to be the case in the continuous Nd^{3+} maser,[9] whereas in the continuous ruby maser[10] the relaxation oscillations are observed to persist indefinitely.

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†The first announcement of the continuous operation of the $CaF_2:U^{3+}$ maser was made at the January, 1962 meeting of the American Physical Society in New York.

[1]L. N. Galkin and P. P. Feofilov, Doklady Akad. Nauk S.S.S.R. 114, 745 (1957) [translation: Soviet Phys.—Doklady 2, 255 (1957)].

[2]L. N. Galkin and P. P. Feofilov, Optics and Spectroscopy 1, 492 (1959).

[3]P. P. Sorokin and M. J. Stevenson, Phys. Rev. Letters 5, 557 (1960).

[4]P. P. Sorokin and M. J. Stevenson, Advances in Quantum Electronics (Columbia University Press, New York, 1961), pp. 65-76.

[5]P. A. Miles, Advances in Quantum Electronics (Columbia University Press, New York, 1961), comment on page 76.

[6]B. Bleaney, P. M. Lewellyn, and D. A. Jones, Proc. Phys. Soc. (London) B69, 858 (1956).

[7]A. Yariv (to be published).

[8]G. D. Boyd and J. P. Gordon, Bell System Tech. J. 40, 489-507 (1961).

[9]L. F. Johnson, G. D. Boyd, K. Nassau, and R. R. Soden, Proc. Inst. Radio Engrs. Corres. 50, 213 (1962).

[10]D. F. Nelson and W. S. Boyle, J. Appl. Optics (to be published).

TEMPERATURE OF THE TRANSITION TO THE SUPERCONDUCTING STATE

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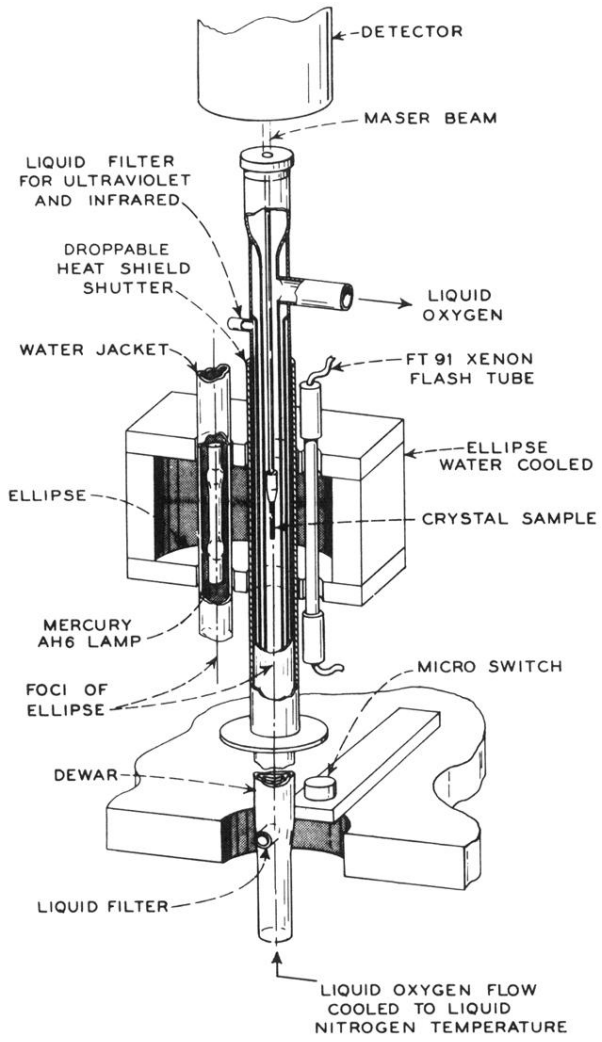
The ordinates of Fig. 1 are "observed" values of the Bardeen-Cooper-Schrieffer (BCS) parameter $[N(0)V]$ for various metals, derived by the usual formula expressing the transition temperature of a superconductor.[1] Where superconductivity has not been detected, the point of the arrow rests on the maximum value that $[N(0)V]$ can have if there is, in fact, a transition to superconductivity below the lowest temperature which has so far been investigated for that metal.[2] The point for Bi refers to the superconducting transition observed in films condensed at very low temperatures.[3]

Along the horizontal axis is plotted

$$[N(0)V]_{\text{theory}} = 3Z\frac{m}{M}\left(\frac{\mathfrak{u}}{k\Theta}\right)^2 + \lambda' - \mu^*, \qquad (1)$$

where Z is the valency, M the mass of an atom, and Θ the Debye temperature of the metal.[1] We take $(\lambda' - \mu^*) = 0.1$ for all metals. The value of $\mathfrak{u}$ is derived from the measured electrical resistiv-



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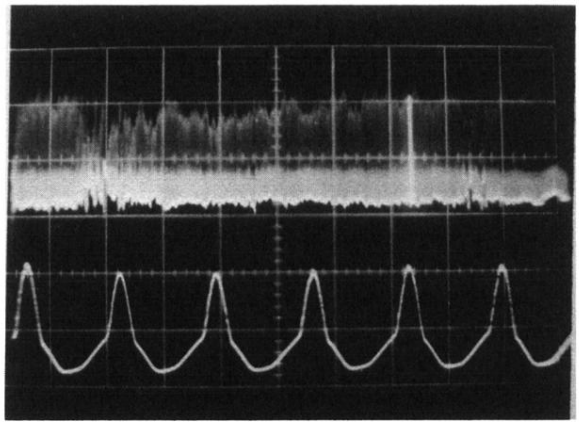
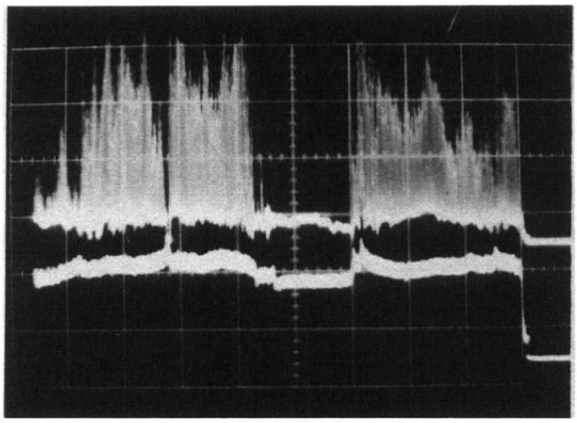


(a)



(b)

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