

# Quartz Resonators; Reduction of Transient Frequency Excursion Due to Temperature Change

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# Communications

## Excitation of the $\text{Nd}^{3+}$ Fluorescence in $\text{CaWO}_4$ by Recombination Radiation in GaAs

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(Received 6 August 1962)

THIS note reports the excitation of the  $1.06\text{-}\mu$  Nd ion fluorescence in  $\text{CaWO}_4$  by recombination radiation from a GaAs  $p$ - $n$  junction. This observation can have important consequences in the attainment of a high efficiency laser operation, and in the simplification and miniaturization of practical laser devices.

The  $1.06\text{-}\mu$   $\text{Nd}^{3+}$  ion fluorescence may be produced by excitation of the ion to the states which comprise the  $^4F_3$  metastable multiplet.<sup>2</sup> The latter lies approximately  $11 \times 10^3 \text{ cm}^{-1}$  ( $8700 \text{ \AA}$ ) above the ground state. Figure 1(a) shows the excitation spectrum of the  $1.06\text{-}\mu$  fluorescence for Nd:CaWO<sub>4</sub> at 77° and 300°K in the region from 8000 to 9000 Å. Of particular interest is the fact that absorption of radiation in the range from about 8650 to 8900 Å will produce the  $1.06\text{-}\mu$  fluorescence.

Recently<sup>3-5</sup> it has been found that GaAs  $p$ - $n$  junctions at 77°K are highly efficient sources of recombination radiation with most of the photon energy concentrated near the band gap energy ( $\sim 1.4 \text{ eV}$ ). We have found that the spectral characteristics of this radiation appear to depend on the method of junction formation, the purity of the GaAs, and the temperature of operation. Figure 1(b) shows some spectra of the recombination radiation that have been observed in our laboratory. The origin of the differences between the various spectra are as yet unknown. However, the important feature is that for some of the samples a major portion of the recombination radiation spectrum lies within the 8650–8900 Å interval and can be used to pump the  $1.06\text{-}\mu$  Nd fluorescence ion.

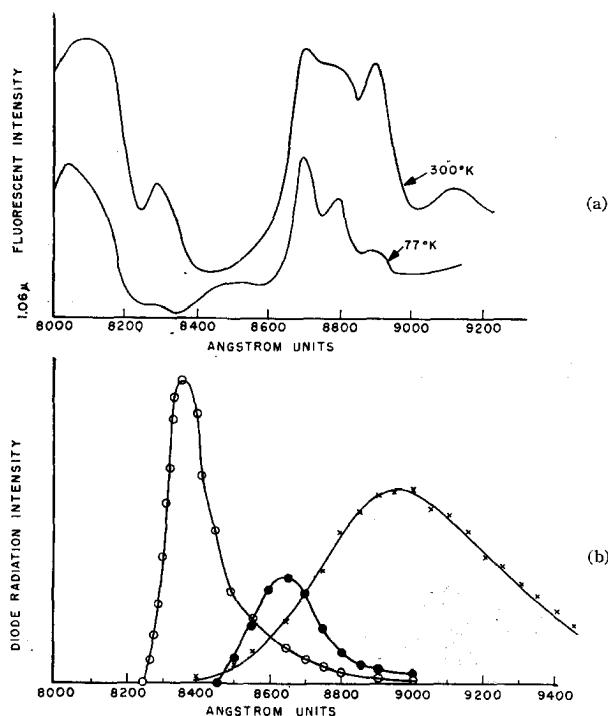


FIG. 1. (a) The excitation spectrum of the Nd:CaWO<sub>4</sub> fluorescence at  $1.06 \mu$  at 300° and 77°K. (b) Some recombination radiation spectra observed from GaAs  $p$ - $n$  junctions operated at 77°K. ○: alloyed junction, 1 A; ●: alloyed junction, 2 A; and ×: diffused junction, 200 mA.

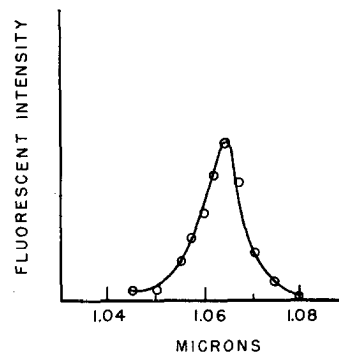


FIG. 2. The fluorescence spectrum of Nd:CaWO<sub>4</sub> at 77°K when excited by the recombination radiation of a Mn-diffused GaAs diode.

In Fig. 2 we show the  $1.06\text{-}\mu$  fluorescence spectrum of Nd:CaWO<sub>4</sub> excited by the recombination radiation from a GaAs diode. The optical arrangement used for the experiment was crude and in consequence the spectrum was obtained under conditions of poor resolution. The figure is solely shown as proof of the principle. Further work will be required to understand and control the recombination radiation spectrum in order to achieve optimum excitation.

The potential advantages of this type of pumping source for a laser are several. The small size and simple structure of the diodes will make possible a direct coupling of the pumping radiation to the laser without any complex optics. This in turn will greatly reduce the size and cost of the functional devices. The efficiency of conversion of input power to output power, both as regards the pump source and the internal conversion of energy within the laser, may permit continuous power output several orders of magnitude higher than is presently possible.

I should like to thank S. Stopek for furnishing the Mn-diffused diode and H. Minden for helpful discussions and for furnishing some diodes used in the work.

<sup>1</sup> L. F. Johnson, G. D. Boyd, K. Nassau, and R. R. Soden, Phys. Rev. 126, 1406 (1962).

<sup>2</sup> E. H. Carlson and G. H. Dieke, J. Chem. Phys. 29, 229 (1958).

<sup>3</sup> R. J. Keyes, T. M. Furst, 1962 Solid State Device Research Conference IRE-AIEE (unpublished).

<sup>4</sup> W. F. J. Hare, M. Gershenzon, and J. M. Whelan, 1962 Solid State Device Research Conference IRE-AIEE (unpublished).

<sup>5</sup> J. I. Pankove and M. Massoulié, Bull. Am. Phys. Soc. 7, 88 (1962); Electro-Chemical Society Extended Abstracts 11, No. 1, 71 (1962); 1962 Solid State Device Research Conference IRE-AIEE (unpublished).

## Quartz Resonators; Reduction of Transient Frequency Excursion Due to Temperature Change

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(Received 17 August 1962)

STUDY of the fractional frequency change  $(\Delta f/f)$  with time ( $t$ ) at temperature ( $\theta$ ), or aging, of AT-cut quartz crystal resonators for frequency standards<sup>1</sup> had indicated that in the first few months of operation aging is often a first-order rate process, i.e.,

$$d/dt(\Delta f/f)_{\theta} = -K_{\theta}(\Delta f/f)_{t, \theta},$$

where  $K_{\theta}$ , the first-order specific aging rate obeys the Arrhenius relation

$$K_{\theta} = K_0 \exp(-Q/R\theta),$$

where  $K_0$  is a constant,  $Q$  the activation energy,  $R$  the gas constant, and  $\theta$  is in degrees Kelvin. Experimentally  $K_{\theta} = 7 \times 10^{-3} \text{ h}^{-1}$  for  $\theta = 50^\circ$  and  $Q$  is about 1 kcal/mole.

Acting on the hypothesis that this aging is caused by relaxation of an interfacial stress between the vapor plated electrode and the quartz surface, it was predicted that resonators without electrodes, or with electrodes which recrystallize at the operating tempera-

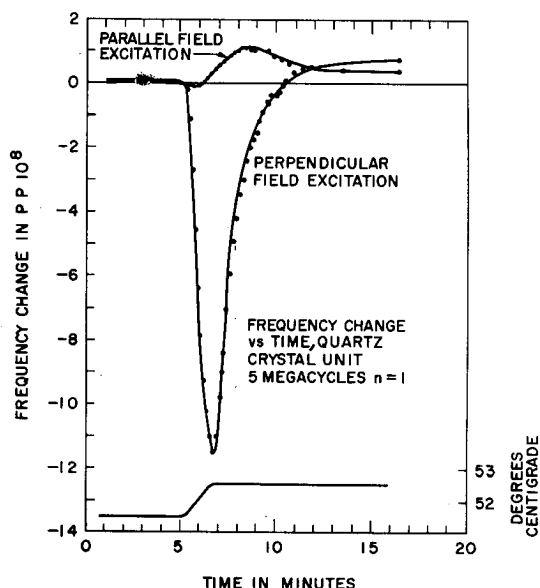


FIG. 1. Transient frequency excursions of perpendicular and parallel field excited AT-cut quartz resonators, subjected to 1-°C temperature change.

ture, should be much less sensitive to their thermal history or to temperature disturbance.

The prediction is being borne out experimentally. The transient frequency excursion of 5-Mc fundamental mode AT-cut plates subjected to 1-°C thermal shocks is decreased over an order of magnitude when the plate is driven by an electric field parallel rather than perpendicular to the major quartz surface. (See Fig. 1.)

This observation supports the hypothesis, since crystals excited in a parallel field do not have electrode metal overlying the frequency determining volume of the plano-convex quartz plate.<sup>2</sup>

The total fractional frequency change of  $10^{-8}$  due to 1-°C temperature cycling makes possible the use of less complex ovens for stabilities of this order.

<sup>1</sup> A. W. Warner Bell System Tech. J. **39**, 1193 (1960).

<sup>2</sup> C. D. Stockbridge and A. W. Warner, *Vacuum Microbalance Techniques* (Plenum Press, New York, 1962), Vol. 2, pp. 71-114.

## Metal Transfer and the Wedge Forming Mechanism

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(Received 7 November 1962)

RECENT papers<sup>1-3</sup> have described sliding mechanisms by which a wedge, or prow, of metal may form and grow between dry or poorly lubricated metal surfaces. The material which forms the wedge originates primarily in the surface having the larger sliding area when specimen geometry is unsymmetrical, i.e., the flat in a rider-flat system or the rotating member of an apparatus having specimens of similar diameter crossed at right angles to each other. If wedge forming metals are compared, it is evident that wedge size is inversely related to metal hardness. However, there are exceptions to this mechanism, and this letter reports a metal sliding system, indium, which does not form wedges.

Sliding experiments were made with a rider-flat apparatus<sup>2</sup> at various speeds from 0.05 to 1 cm/sec and at loads in the range, 2-20 g. The purity of the indium riders and flats was 99.999%. The  $\frac{1}{8}$ -in.-diam riders were hemispherically ended, and the flats were 0.050 in. thick, supported by a hard backing.

In sliding, the riders suffer extensive cold flow. Metal is displaced on them in the direction of motion almost from the initiation of rubbing. Adhesion and metal transfer from rider to flat is very severe. Photomicrographs of a worn rider and flat after approximately 10 mm of sliding are shown in Fig. 1. A freshly turned copper rider pressed against an indium flat likewise slides without the formation of wedges, although indium transfer to it is evident when the parts are separated.

The salient difference between indium and the wedge forming metals, such as Cu, Al, Au, and Pd probably lies in its lack of work hardenability at the room temperature conditions of the experiment. To confirm the inability of indium to work harden, microhardness measurements with a Knopp indenter were made at loads of 5 and 10 g of unworn indium and in wear tracks of the indium flat from an extended run at 10 g with the copper rider. Identical values, close to the literature value of 1 kg/mm<sup>2</sup>,<sup>4</sup> were obtained. Metals which do form wedges show a marked work-hardening capability. This is illustrated in Table I for silver from a 500-revolution run at 100 g and 1 cm/sec with the same apparatus.

It is suggested that in wedge formation, work-hardened transfer metal forms a prow which gouges the flat on continued sliding. Metal ploughed from the flat adheres to the prow, so that the

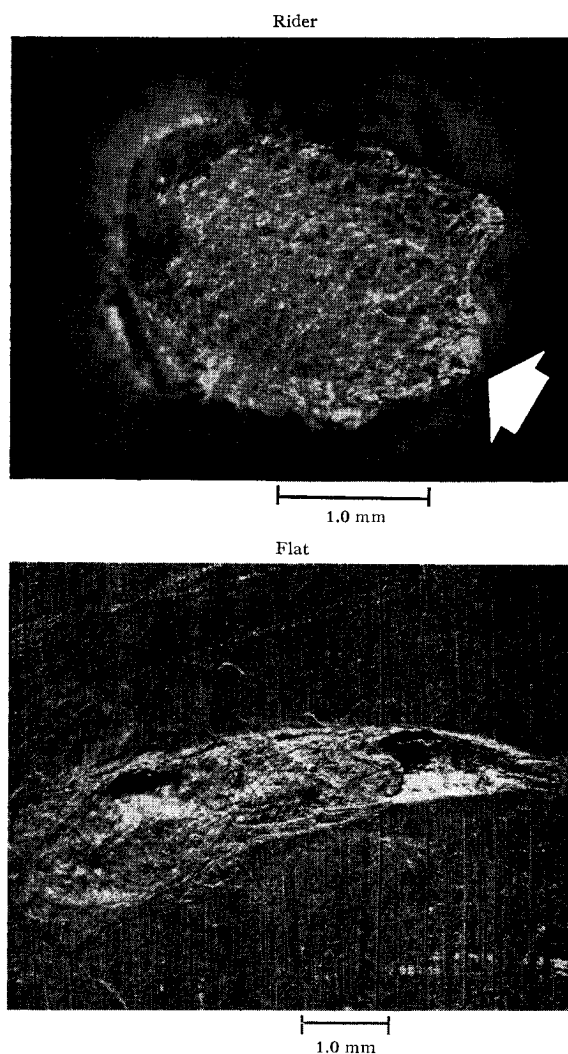


FIG. 1. Indium rider and flat. Sliding distance, approximately 10 mm; load, 10 g; velocity, 0.05 cm/sec. Coefficient of adhesion, approximately 125. Direction of sliding, left to right. Note displaced metal on rider and extensive transfer from rider to flat.