

Shock-Wave Compression of Germanium from 20 to 140 kbar*

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THE object of this note is to report stress-volume results between 20 and 140 kbar for germanium, shock loaded in a state of one-dimensional strain along the [111] crystallographic direction. Resistance-time measurements, made while the shock wave traverses the sample, circumvent difficulties inherent in the usual free surface velocity methods.

Shock loading was accomplished by impacting large diameter-to-thickness ratio disks of germanium upon each other in order to ensure a state of one-dimensional strain in all but the periphery of the disks for the duration of the experiment. One disk, mounted on the face of a projectile, was accelerated to a measured high velocity by means of a compressed gas gun¹ and was impacted in vacuum upon the specimen disk mounted on the end of the gun. Angular misalignment between the impacting surfaces was about 5×10^{-4} rad.² Germanium back-up disks were mated to the rear of the specimen. The thicknesses of the impact and back-up disks were chosen so that the stress waves propagated through and out of the specimen disk without reflection until, finally, the specimen was stressed uniformly to the impact value for a brief interval preceding the arrival of unloading waves.

The disks, 38 mm in diameter, were cut from single crystals of high purity *n*-type germanium of nominal 50- Ω -cm resistivity and were oriented with their faces parallel to a (111) crystal plane. Their dislocation density was approximately $6 \times 10^8/\text{cm}^2$. Depending on the particular experiment, the thicknesses of the specimen disks were 3.2, 4.0, and 8.0 mm.

The resistance-time history resulting from stress waves propagating through the specimen was obtained by recording the voltage-time history across the thickness of the specimen disk under constant current conditions. The constant current of one ampere was applied to the specimen disk about 500 nsec before impact to prevent resistive heating of the disk. Both faces of the disk were entirely electroless nickel plated to provide Ohmic electrodes. The impact surface electrode of the specimen was also coated with vapor deposited silver and maintained at ground potential. The back-up disk assembly, entirely vapor coated with silver, served as the circuit lead to the other electrode.

For impact stresses in the range of several hundred kilobars, multiple waves are observed which indicate the presence of slope discontinuities, or cusps, in the stress-volume relation.³ During the time these waves are propagating across the specimen thickness, the specimen is essentially divided into a number of zones separated by the different wave fronts. Thus, the electrical resistance between the electrodes of the specimen is equal to the sum of the resistances of the zones. Assuming time independent wave velocities, stress amplitudes, and resistivities, the initial

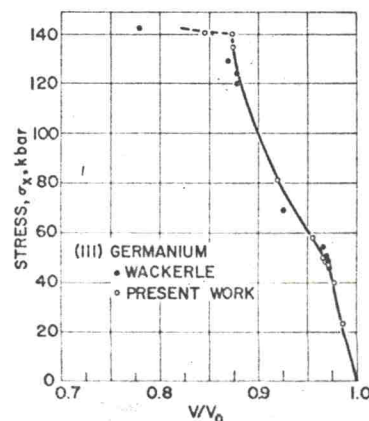
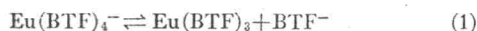


FIG. 1. Stress-volume relation.

ions are negligible compared to the anion. Therefore, "blocking" of laser pump light by the cations does not take place to important extent.

The absolute quantum efficiency of the piperidinium salt (0.05M in acetonitrile, irradiated with 3150 Å light) has been measured by comparison with rhodamine B as a standard^{3,4} and found to be 0.75 ± 0.15 . The ratio of the quantum efficiency of the quinolinium to the piperidinium salt solution is, however, 0.65. At room temperature about 95% of the total fluorescence of both solutions occurs near 6120 Å in the $^5D_0 \rightarrow ^7F_2$ transition characteristic of Eu^{+3} .

A possible reason for the lower quantum efficiency of the quinolinium salt solution involves quenching of the anion emission by interaction with the quinolinium ion. If such a process is operative, one would expect the quantum efficiency to decrease as the concentration of the chelate salt in solution is increased. However, while the quantum efficiency of the piperidinium salt remained constant on increasing the concentration from 5×10^{-3} to 10^{-1} M, that of the quinolinium salt increased about 18%. This fact indicates that such a quenching process is not taking place. An alternate explanation for the lower quantum efficiency of the quinolinium salt, which is consistent with the observed results, can be given in terms of the dissociation of the chelate anion, reaction (1).



The quantum efficiency of the electrically neutral tris chelate $\text{Eu}(\text{BTF})_3$ in acetonitrile is only about $\frac{1}{10}$ that of $\text{PEu}(\text{BTF})_4$ solutions. Any dissociation according to (1), therefore, results in lower over-all quantum efficiencies.

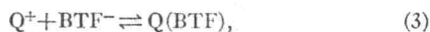
Since the $^5D_0 \rightarrow ^7F_2$ emission band for $\text{Eu}(\text{BTF})_3$ occurs at nearly the same wavelength as for $\text{PEu}(\text{BTF})_4$, the presence in solution of $\text{Eu}(\text{BTF})_3$ is more easily detected by means of much weaker $^5D_0 \rightarrow ^7F_0$ emissions. Figure 1 shows this portion of the fluorescence spectrum for solutions made up from $\text{PEu}(\text{BTF})_4$, $\text{Eu}(\text{BTF})_3$, and $\text{QEu}(\text{BTF})_4$, where Q is the quinolinium ion. From the nearly symmetrical shape of the main peak of curve (a) and the relative intensities of curves (a) and (b), the amount of $\text{Eu}(\text{BTF})_3$ in the solution prepared from $\text{PEu}(\text{BTF})_4$ is found to be less than 10% of the total europium present. Curve (c), however, shows an asymmetry which we attribute to the presence of appreciable $\text{Eu}(\text{BTF})_3$.

If *f* represents the fractional dissociation of tetrakis molecules in the quinolinium solution and *r* the ratio of the intensity of the $^5D_0 \rightarrow ^7F_0$ emission from tris molecules in the quinolinium solution (c) to that from the pure tris solution (b), we have⁵

$$r = 3/4f. \quad (2)$$

Constructing curve (c) from the sum of two appropriate curves of type (a) and (b), we find *f* to be equal to 0.40.

The greater amount of $\text{Eu}(\text{BTF})_3$ observed in solutions prepared from $\text{QEu}(\text{BTF})_4$ suggests that the quinolinium ion facilitates the dissociation of $\text{Eu}(\text{BTF})_4^-$. We postulate, as one possible mechanism, that this is the result of ion pairing according to reaction (3). To the extent that



occurs, BTF^- is removed from solution and equilibrium (1) is shifted to the right.

In summary, the results presented here show that the cation in the salt $\text{BEu}(\text{BTF})_4$ can be important in determining the laser capabilities of solutions containing the salt without interacting directly with the lasing species $\text{Eu}(\text{BTF})_4^-$ to change its spectral properties.

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¹ H. Samelson, A. Lempicki, C. Brecher, and V. Brophy, *Appl. Phys. Lett.* **5**, 173 (1964).

² J. Schimitschek, J. A. Trias, and R. B. Nehrich, Jr., *J. Appl. Phys.* **36**, 1165 (1965).

³ Weber and F. W. J. Teals, *Trans. Faraday Soc.* **53**, 646 (1957).

⁴ H. Melhuish, *J. Phys. Chem.* **65**, 229 (1961).

⁵ C. Brecher, H. Samelson, and A. Lempicki, *J. Chem. Phys.* **42**, 1081 (1965).

surprising degree in Table I. In addition, the observed room-temperature fluorescence intensity at this temperature and at -30°C .

The solutions containing the quinolinium salt were prepared from a 5×10^{-3} M concentration of the quinolinium salt and a 0.05 M concentration of the europium salt. The results are included in Table I. The quinolinium salt did not

show any fluorescence in a 1-mm cell. The results are included in detail along with the later data.

When the solutions were prepared by combining, in ethyl acetone and the organic solvent, the quinolinium salt and the europium salt, the fluorescence intensity was in satisfactory agreement with the results obtained with the tris chelate $\text{Eu}(\text{BTF})_3$ compound.

The fluorescence quantum yield was not expected to be high. The results indicate that each of the solutions has a quantum yield of the order of 0.1. The fluorescence intensity of the quinolinium salt is of the order of 10% of that of the tris chelate $\text{Eu}(\text{BTF})_3$.

The fluorescence intensity of the solutions was measured in a 1-mm cell. The absorption of the solutions was measured in a 1-cm cell.

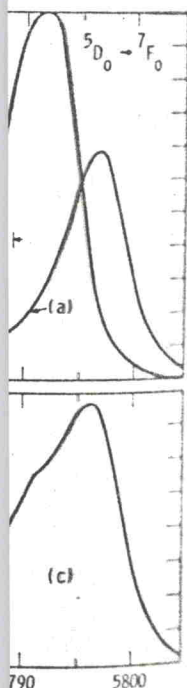


Figure 2. Fluorescence spectra of solutions of $\text{Eu}(\text{BTF})_4$ in acetonitrile.

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The first part of the paper is devoted to a general
 consideration of the problem. It is shown that the
 problem is equivalent to the problem of finding the
 minimum of a certain function. This function is
 defined by the following expression:

$$F(x) = \int_0^x f(t) dt + \int_x^1 g(t) dt$$

where $f(t)$ and $g(t)$ are given functions. The
 minimum of $F(x)$ is found by setting the derivative
 equal to zero. This leads to the equation

$$f(x) = g(x)$$

which can be solved for x . The solution is the
 value of x which minimizes $F(x)$.

The second part of the paper is devoted to a
 detailed study of the case where $f(t)$ and $g(t)$
 are linear functions. In this case the minimum of
 $F(x)$ is found by setting the derivative equal to
 zero. This leads to the equation

$$a + bx = c + dx$$

where $a, b, c,$ and d are constants. The solution
 is

$$x = \frac{c - a}{b - d}$$

provided $b \neq d$. If $b = d$, the minimum is
 found at the boundary values $x = 0$ or $x = 1$.

The third part of the paper is devoted to a
 study of the case where $f(t)$ and $g(t)$ are
 quadratic functions. In this case the minimum of
 $F(x)$ is found by setting the derivative equal to
 zero. This leads to a quadratic equation which
 can be solved for x . The solution is the value
 of x which minimizes $F(x)$.

