PHYSICAL REVIEW B VOLUME 21, NUMBER 2 15 JANUARY 1980

Triboluminescence and the dynamics of crystal fracture

B. P. Chandra* and J. I. Zink

Department of Chemistry, University of California, Los Angeles, California 90024

(Received 6 November 1978; revised manuscript received 22 May 1979)

Triboluminescence appears concurrently with the sudden force decreases in the fracture region of the force versus compression curves of tartaric-acid, sugar, ammonium-tartrate, lithium-sulfate-monohydrate, and citric-acid-monohydrate crystals. This relationship suggests that the motion of cracks and thereby the creation of new surfaces is responsible for the excitation of triboluminescence in these crystals. All of these crystals exhibit triboluminescence from the second positive group of molecular nitrogen. The intensity and time dependence of triboluminescence is measured as a function of the velocity of impact of a piston on single crystals. A quantitative expression for time and impact velocity dependence of the triboluminescence intensity,

$I = (\eta b V u^3 v^3/\alpha^2 h^3) e^{-\alpha t}(1 - e^{-\alpha t})^2 \exp[-(\beta u^2 v^2/\alpha^2 h^2)(1 - e^{-\alpha t})^2]$,

is derived from the movement and the interaction of mobile cracks. This equation explains the observed dependence of the triboluminescence intensity on the impact velocity, the applied stress, the temperature, and the crystal dimensions. The values of α and β are determined from triboluminescence measurements. α is related to the viscosity of the crystal and β is related to the attrition coefficient of mobile cracks in the crystal. The triboluminescence activity decreases over three orders of magnitude from sugar to citric-acid crystals.

I. INTRODUCTION

Triboluminescence is the emission of light produced during mechanical action on solids.[1,2] Although it is an old phenomenon, its mechanism is not well understood. Most triboluminescent crystals exhibit triboluminescence only during their fracture. However, crystals of impurity-doped zinc sulfides and colored alkali halides show triboluminescence in their elastic, plastic, and fracture regions. Because of the complexity of crystal fracture, relatively little progress has been made on the mechanical investigations of triboluminescence. Previous studies were chiefly concerned with the identification of new triboluminescent substances,[3-5] the spectroscopy of triboluminescence,[6-8] and the relationships between triboluminescence and the physical properties of crystals.[9-18] It has been found that the triboluminescence spectra of some crystals resemble the discharge spectra of surrounding gasses, the triboluminescence spectra of some crystals resemble their photoluminescence spectra, and the triboluminescence spectra of some crystals consist of both the gas discharge and photoluminescence spectra.

An essential step in the understanding of triboluminescence, as in all luminescence research, is the establishment of the signal-to-source correlation. As triboluminescence is produced during deformation of a crystal, a correlation between the triboluminescence intensity and the crystal deformation is expected. To date, neither the time dependence of the triboluminescence nor the intensity dependence as a function of crystal deformation is satisfactorily understood. In this paper the time dependence of the triboluminescence intensity as a function of the time dependence of the mechanical excitation is reported and an explanation based on the movement and interaction of mobile cracks is derived. In order to unify the discussion, crystals having only nitrogen-emission triboluminescence are chosen in the present investigation.

II. EXPERIMENTAL

Single crystals of tartaric acid, sugar, ammonium tartrate, lithium-sulfate monohydrate, and citric-acid monohydrate were grown from aqueous solutions of the reagent-grade materials. The crystals used in the stress-strain measurements were reduced to the required size by grinding and polishing.

The instrument used for the excitation of triboluminescence at different impact velocities is based on an air-driven steel piston. The air pressure is variable up to 400 psi. A Hewlett-Packard velocity transducer (Model No. LVSYN6LV1) is attached to the piston to measure its velocity. The calibration constant of the velocity transducer was 0.238 V cm^{-1} sec. Below the piston, there is a vertically adjustable sample holder. The crystal is placed on a lucite or quartz plate inside the sample holder. The luminescence is monitored from below the transparent plate using an IP 28 photomultiplier tube (response time 7 μsec) connected to a Tektronix 564 dual beam storage oscillosope.

To start the experiment, the piston is released and moves under the force of the compressed gas. By changing the pressure, the impact velocity of the piston can be changed from very low values to approximately 500 cm/sec. To trigger the oscilloscope, the crystal is covered with a thin aluminum foil which is connected to one terminal of a 1.5-V battery through a resistance. The other terminal of the battery is connected to the piston. When the piston touches the aluminum foil on the crystal, the pulse which appears across the resistance triggers the oscilloscope. The rise and decay of the luminescence and the velocity of the piston are recorded simultaneously. The total intensity of the triboluminescence is determined from the area below the triboluminescence intensity versus time curve which is measured with a planimeter. The compression of the impact instrument was 0.32, 0.52, 0.63, and 0.76 mm for the impact velocity 63, 210, 315, and 378 cm/sec, respectively.

The triboluminescence spectra were taken using the methods described previously.[19] In this method, the triboluminescence spectra were determined using a Bausch and Lomb 1-m grating monochromator and EMI 9558*RF* photomultiplier tubes which have a nearly flat wavelength response from 300 to 450 nm. No corrections for the response characteristics of the instruments were made.

The simultaneous measurements of the triboluminescence versus compression curves and the force versus compression curves of single crystals were carried out using a table model Instron testing machine fitted with a compression cage. The compression of the crystal was measured using a linear variable differential transducer (LVDT) (Model No. 025 MHR, Schaevitz Engineering Company) whose calibration constant was 2530 mV/mm. The load in the crystal was measured by 907.2-kg capacity Lebow load cell (Model No. 3354-2K) in conjunction with a Viatron signal conditioner (Model No. 603). The calibration constant of the load cell was 6.125 mV/kg. The outputs of the load cell and the LVDT were automatically recorded on a Hewlett-Packard Model No. 7004-A x-y recorder. The triboluminescence produced during deformation of the crystal was monitored by an IP 28 photomultiplier tube placed near the crystal. The amplified outputs of the photomultiplier tube and the LVDT were recorded on a second x-y recorder. The compression of the crystal at any force was determined by subtracting the known machine compression at that force. The triboluminescence versus compression curve of the crystal was determined at the compression rate of 1.69×10^{-3} mm/sec. The time duration of the triboluminescence pulse produced during the motion of a single crack was determined using an IP 28 photomultiplier tube with a response time of 100 nsec connected to the oscilloscope.

III. RESULTS

The rise and decay of the triboluminescence of a single crystal of tartaric acid at high impact velocity is shown in Fig. 1. The lower trace is the output of the velocity transducer. The upper trace is the photomultiplier output. The triboluminescence appears only after the impact of the piston with the crystal, reaches its maximum intensity a few tenths of a millisecond after the impact, and then decays. For high impact velocities the piston moves with an approximately constant velocity during the appearance of triboluminescence and stops suddenly after the triboluminescence has ceased. However, for low impact velocities, the piston moves with decreasing velocity with increasing time after the impact.

The variations of intensity (I) of the triboluminescence with time in tartaric-acid crystals for different impact velocities is shown in Fig. 2. The maximum in the triboluminescence intensity versus time curve increases in intensity with increasing impact velocity. The maximum shifts towards smaller time values with increasing impact velocities. For a given impact velocity, the peak of the triboluminescence versus time curve increases and shifts towards larger time values with increasing size of the crystal.

The force versus compression curve and the triboluminescence versus compression curve of a $7\times2\times9$ mm^3 single crystal of tartaric acid is shown in Fig. 3. The triboluminescence appears only during the steps which occur in the force versus compression curve of the crystal.

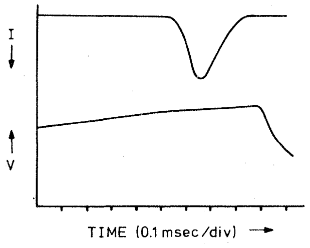

FIG. 1. Time dependence of the triboluminescence intensity (top) and the velocity of piston (bottom), for a tartaric-acid crystal.

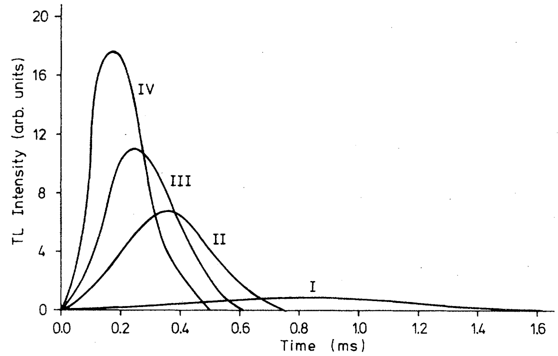

FIG. 2. Time dependence of triboluminescence of (TL) in 4.5×4.0×1.5 mm^3 tartaric-acid crystals at impact velocities of (I) 38 cm/sec, (II) 168 cm/sec, (III) 252 cm/sec, and (IV) 378 cm/sec.

The maximum intensity (I_m) of the triboluminescence in a triboluminescence vs time curve increases with the impact velocity as shown in Fig. 4(a). Figure 4(b) shows that the total integrated intensity of triboluminescence increases and attains a saturation value at the higher values of the impact velocity.

Figure 5(a) shows the variation of the peak of triboluminescence intensity versus time curve with mass of the crystals for a constant impact velocity of 399 cm/sec. Figure 5(b) shows the variation of the total intensity of triboluminescence with the mass of the crystals for the impact velocity 399 cm/sec.

The total intensity per g-mole of a crystal was calculated from the total intensity of triboluminescence for a known mass of a crystal at the impact velocity 399 cm/sec. Table I shows the relative intensity of triboluminescence per g-mole of crystals normalized with respect to that of sugar crystals. No significant changes in triboluminescence activity are found with respect to the crushing direction of the crystals.

Figure 6 shows the triboluminescence spectra of tartaric-acid crystals. The triboluminescence spectra of tartaric-acid crystals correspond within the limit of resolution of the experiment to the second positive group ($^3\Pi_u - {}^3\Pi_g$) of molecular nitrogen.[20] The spectra of the other crystals studied here are identical within experimental error to that of tartaric-acid crystals.

The half width of a triboluminescence pulse due to the motion of a single crack was found to be

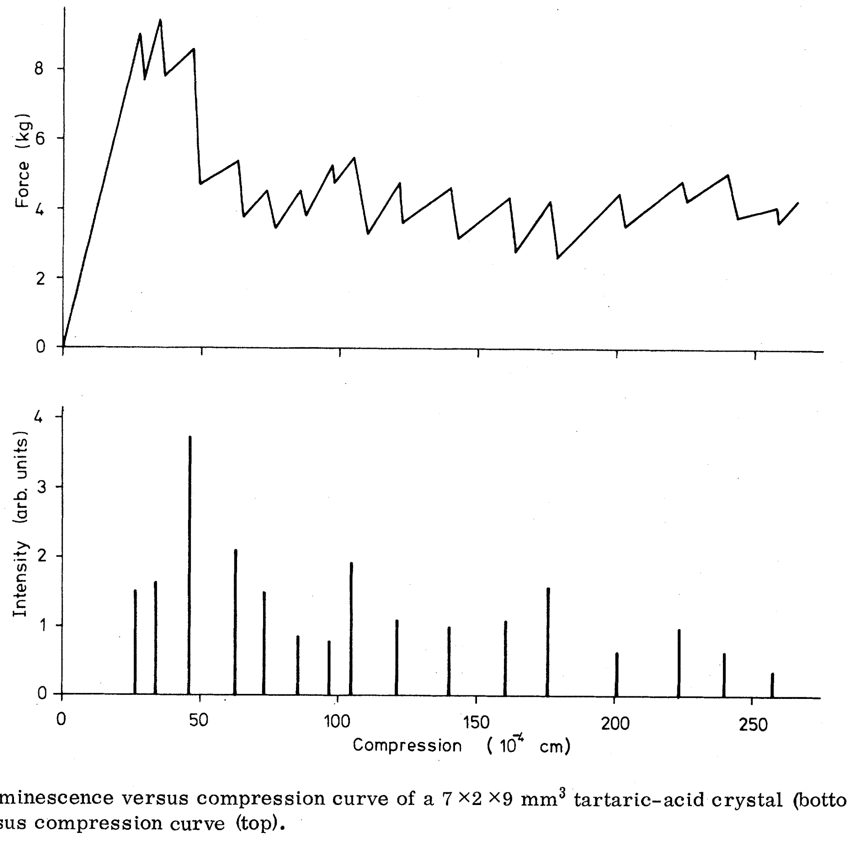

FIG. 3. Triboluminescence versus compression curve of a 7×2×9 mm^3 tartaric-acid crystal (bottom) and its simultaneous force versus compression curve (top).

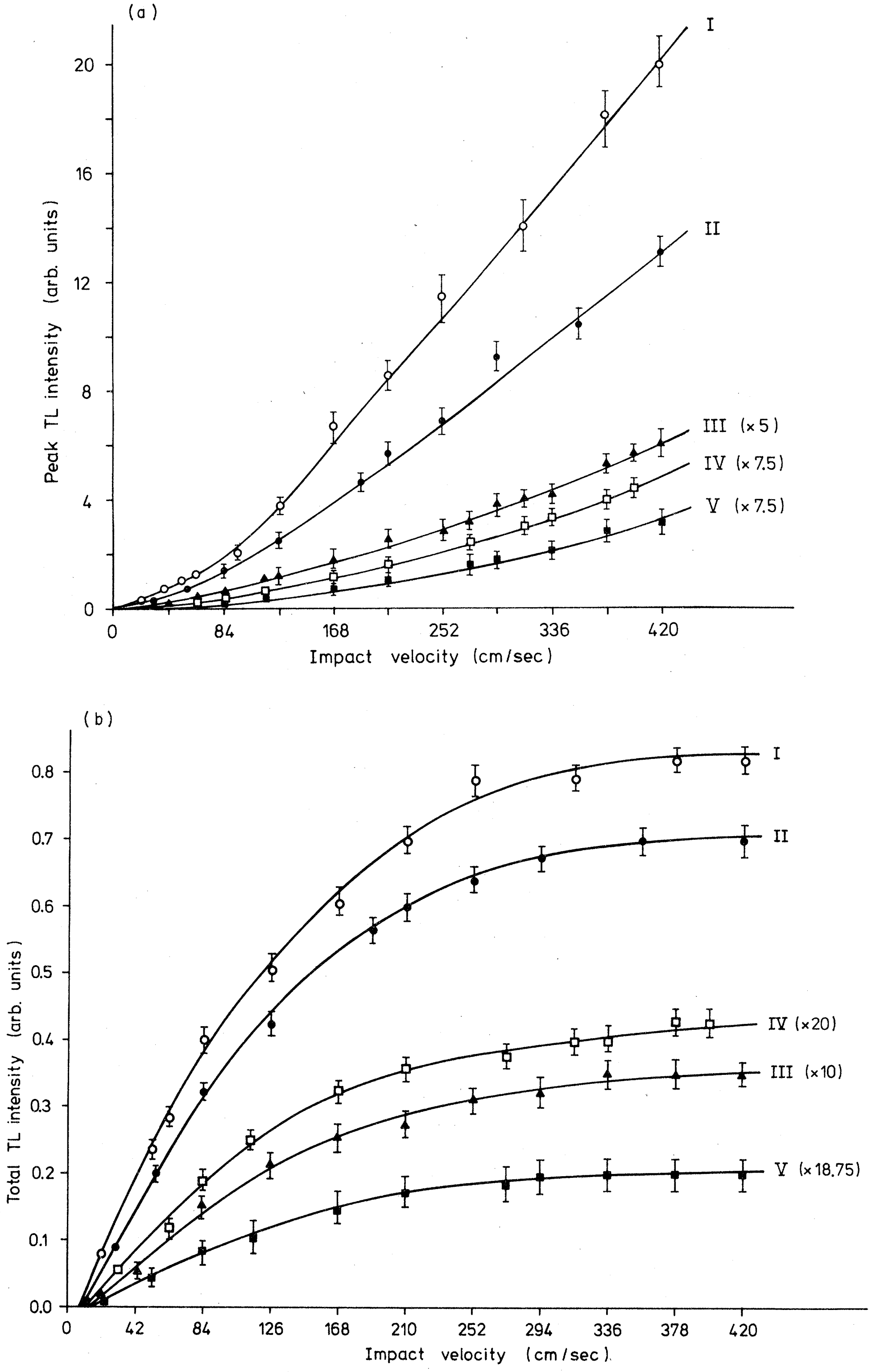

FIG. 4. Dependence of (a) the peak intensity of the triboluminescence and (b) the total integrated intensity of the triboluminescence on the impact velocity. (I) Tartaric acid, (II), sugar, (III), lithium sulfate, (IV) ammonium tartrate, (V) citric acid.

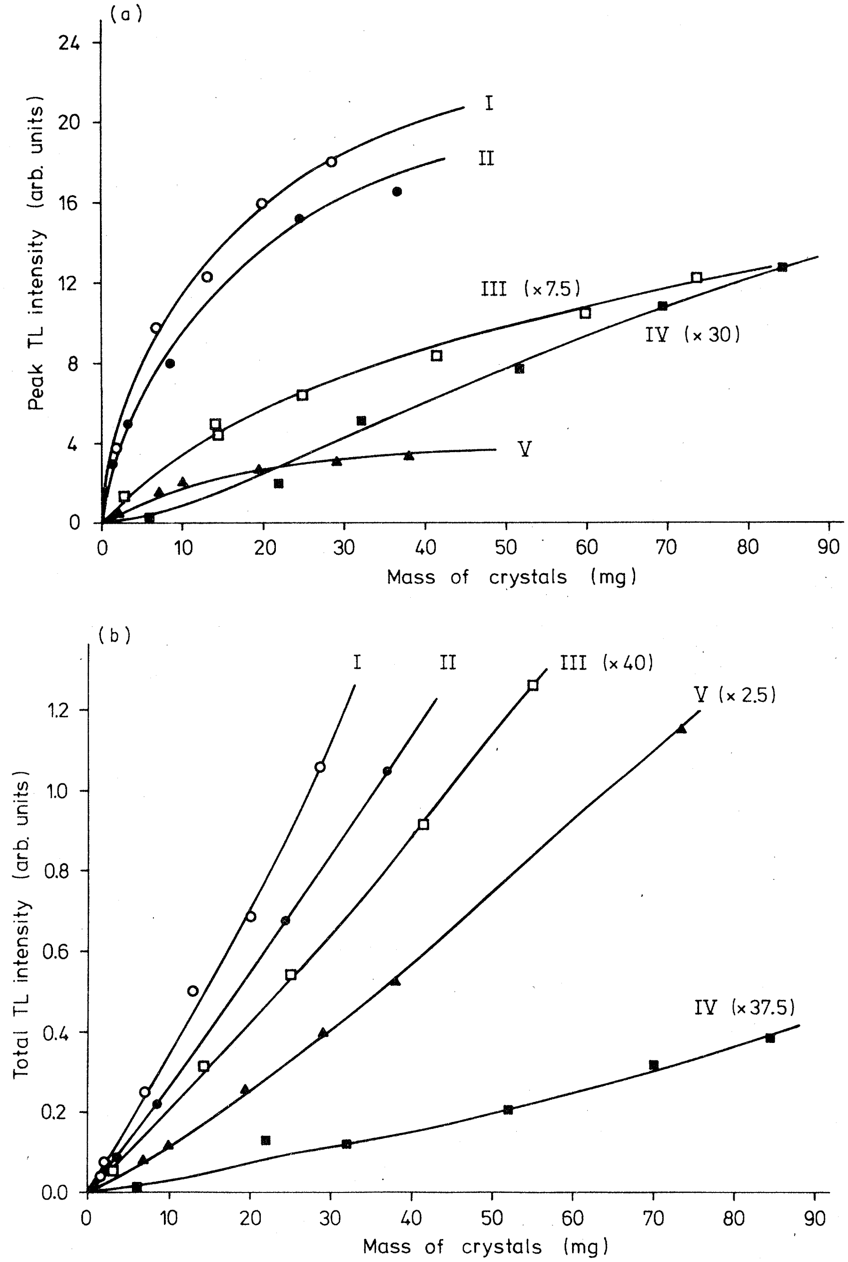

FIG. 5. Dependence of (a) the peak intensity of the triboluminescence versus time curves and (b) the total integrated intensity of triboluminescence on the mass of the crystals. (I) Tartaric acid, (II) sugar, (III) ammonium tartrate, (IV) citric acid, (V) lithium sulfate.

4.5 ± 0.5, 5.5 ± 0.5, and 4 ± 0.5 μsec for tartaric-acid, sugar, and lithium-sulfate crystals, respectively. The dimensions of tartaric-acid, sugar, and lithium-sulfate crystals were $7 \times 7 \times 3.5$, $4 \times 4 \times 3$, and $4 \times 4 \times 2.5$ mm^3, respectively. The half width of the triboluminescence pulse due to the motion of a single crack decreases with decreasing size of the crystals and also decreases with the subsequent increase in the number of cracks in a crystal when the crystal is repeatedly cracked.

Figure 7 shows that for the high impact velocities the plot of $\log(I/t^2)$ versus t^2 is linear with a negative slope and a correlation factor between

TABLE I. Values of important constants of crystals determined from and related to triboluminescence (TL) measurements.

Crystal	Size (mm^3)	Crushing direction (crystallographic axis)	Value of β	Value of α from triboluminescence measurements	Value of α from logarithmic decrement of v	Piezoelectric constants (d_{22}) (10^8 esu/dyne)	Normalized TL activity per g-mole with respect to that of sugar crystals
Sugar	4 × 2.3 × 2.3	b	13.5 ± 0.5	941 ± 39	933 ± 50	−10.25 (Ref. 28)	1.00
Tartaric acid	4.5 × 4 × 1.5	b	12.4 ± 0.4	1002 ± 46	945 ± 53	−6.5 (Ref. 29)	0.58 ± 0.04
Ammonium tartrate	3 × 2 × 2	c	15.8 ± 0.8	1026 ± 49	1155 ± 64	−26.2 (Ref. 30)	$(1.1 \pm 0.1) \times 10^{-2}$
Lithium-sulfate monohydrate	2 × 1.5 × 1	c	21.9 ± 1.1	1597 ± 73	1565 ± 78	45.0 (Ref. 29)	$(5.8 \pm 0.4) \times 10^{-2}$
Citric-acid monohydrate	5 × 4 × 2.9	a	19.3 ± 2.0	900 ± 50	1020 ± 65		$(2.2 \pm 0.2) \times 10^{-3}$

0.95 and 1.0, which suggests the relation

$$I = I_0 t^2 \exp(-\gamma t^2)\ . \tag{1}$$

The physical meaning of the parameters I_0 and γ will be discussed below. The slope γ increases with the impact velocity v and decreases with the thickness of the crystal.

IV. DISCUSSION

A. Time dependence of triboluminescence

The steps in the fracture region of the force versus compressions curve (Fig. 3) are caused by the movement of cracks in the crystal and the sudden creation of new surfaces.[21] The surface energy of the crystals increases. The appearance of triboluminescence only when the steps occur in the force versus compression curve of a crystal suggests that the triboluminescence in these crystals requires the motion of cracks. The time duration of the triboluminescence pulse due to the motion of a single crack is in the microsecond range, which is of the order of the time needed for a crack to move through the crystal. However, the time duration of a continuous triboluminescence pulse produced during the fracture of a crystal is of the order of milliseconds and depends on the impact velocity. Thus, the continuous triboluminescence signal produced during the impact is the superposition of individual triboluminescence pulses produced during the motion of many cracks in the crystal. The time dependence of triboluminescence produced during impact of a piston with the crystal will be described phenomenologically in terms of the number of mobile cracks.

Let dN be the number of cracks produced during the change of strain from ϵ to $\epsilon + d\epsilon$. Then dN may be written as

$$dN = M d\epsilon\ , \tag{2}$$

where M is the correlation factor between the number of cracks and the strain of the crystals.

When a crystal is compressed, its volume will change linearly with the strain and consequently the number of point defects in the crystal will increase with the strain.[22] Because the increase in the number of point defects will increase the probability of nucleation of cracks in a crystal, the correlation factor M will increase with the strain of the crystal. Thus dN may be given by

$$dN = M_0 \epsilon d\epsilon\ , \tag{3}$$

where M_0 is constant.

From the above equation, the total number of cracks may be given by

$$N_T = \tfrac{1}{2} M_0 (\epsilon^2 - \epsilon_f^2)\ , \tag{4}$$

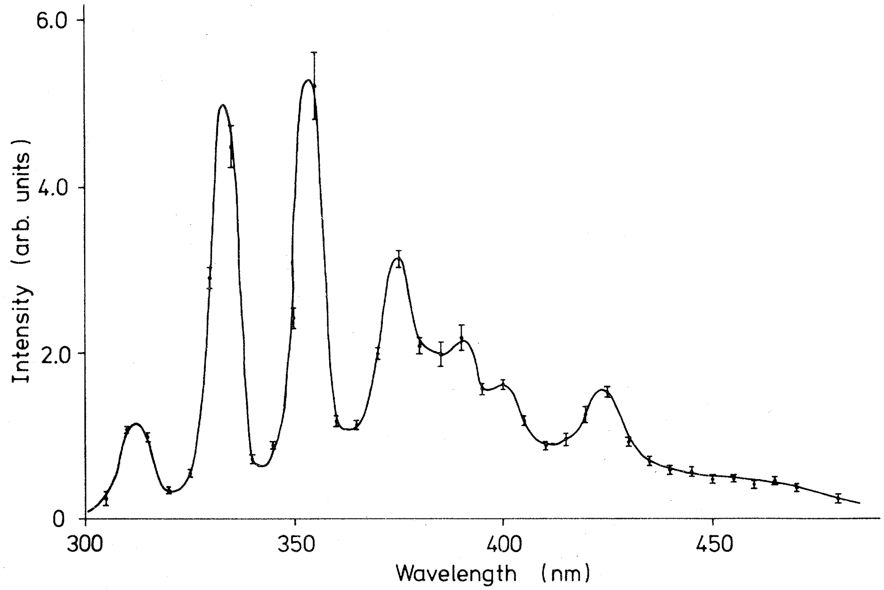

FIG. 6. Triboluminescence spectrum of tartaric-acid crystals obtained using the instrument described in Ref. 19.

where ϵ_f is the strain needed to fracture a crystal. Because the total number of cracks will be directly proportional to the volume V of the crystal, the above equation may be written as

$$N_T = bV(\epsilon^2 - \epsilon_f^2)\,, \tag{5}$$

where M_0 is $2bV$.

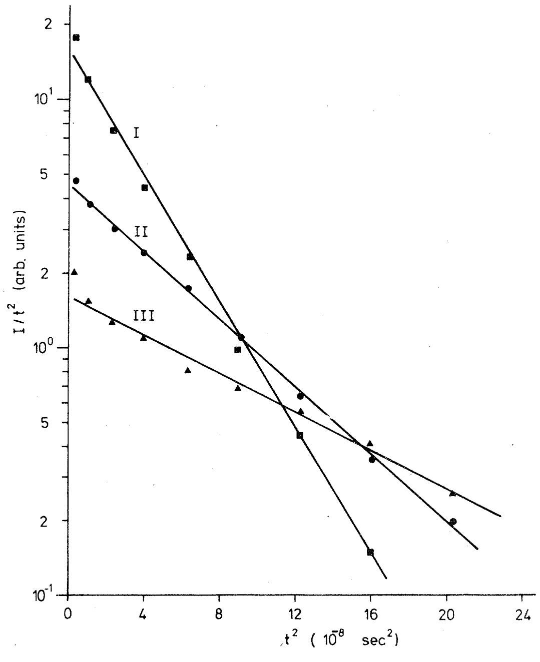

FIG. 7. Plot of $\log(I/t^2)$ vs t^2 for different impact velocities on $4.5 \times 4 \times 1.5$ mm^3 tartaric-acid crystals. (I) 378 cm/sec, (II) 252 cm/sec, (III) 168 cm/sec.

The left-hand side of Eq. (5) is related to the area of new surfaces created during the fracture of a crystal, and the right-hand side is related to the mechanical energy given to the crystal minus the threshold energy for the fracture of the crystal. The above equation is in accordance with the energy condition for the instability of cracks in a crystal[23] which states that after the threshold energy of fracture, the area of new surfaces created is directly proportional to the energy of the crystal.

Only a fraction f of the total number of cracks will remain mobile. The number N_m of mobile cracks will be fN_T. As N_T increases, the fraction f will decrease due to the interaction between the cracks. Assuming a first-order rate process for the decrease of f with N_T per unit volume, f may be written as

$$f = \exp\left(-\frac{\lambda N_T}{V}\right), \tag{6}$$

where λ is a constant related to the interaction between the cracks.

The above discussion suggests the following equation for the strain dependence of the number of mobile cracks:

$$N_m = bV(\epsilon^2 - \epsilon_f^2)\exp[-\beta(\epsilon^2 - \epsilon_f^2)]\,, \tag{7}$$

where β is equal to λb.

If the triboluminescence emission is excited by the motion of cracks, the number of triboluminescence centers excited in the strain range from ϵ to $\epsilon + d\epsilon$ will be proportional to the probability $N_m(\epsilon)d\epsilon$ of the creation of mobile cracks in the strain range. Thus, the number of excited triboluminescence centers during the change of the strain from ϵ to $\epsilon + d\epsilon$ may be written as

$$dn = \eta N_m d\epsilon$$

or

$$\frac{dn}{d\epsilon} = \eta b V(\epsilon^2 - \epsilon_f^2)\exp[-\beta(\epsilon^2 - \epsilon_f^2)] , \tag{8}$$

where η is the normalization constant which takes into account the triboluminescence activity of the crystal.

If the strain ϵ is measured after the fracture of the crystal, that is, after the appearance of triboluminescence, the term $\epsilon^2 - \epsilon_f^2$ can be replaced by ϵ^2 and the above expression may be written as

$$\frac{dn}{d\epsilon} = \eta b V \epsilon^2 \exp(-\beta\epsilon^2) . \tag{9}$$

Our interest is to interpret the time dependence of the triboluminescence signal obtained during fracture of the crystal. For this purpose, we have to determine how the compression of a crystal depends on the impact velocity and how it increases with the time after the impact. The velocity of the piston decreases with the compression of the crystal and the equation of its motion may be given by

$$\frac{d\kappa}{dt} + \alpha\kappa = 0 , \tag{10}$$

where κ is the compression of the crystal and α is the rate constant of compression of the crystal. After integration, Eq. (9) may be written as

$$\kappa = \kappa_0(1 - e^{-\alpha t}) , \tag{11}$$

where κ_0 is the maximum compression.

Equation (11) shows that the compression rate of the crystal is $d\kappa/dt = \kappa_0\alpha e^{-\alpha t}$. If the initial velocity of impact of the piston is v, then $\kappa_0\alpha$ should be equal to v and Eq. (11) may be written as

$$\kappa = \frac{v}{\alpha}(1 - e^{-\alpha t}) . \tag{12}$$

If crystals of small dimensions are chosen the compression of the impact instrument becomes considerable and the real compression of the crystal may be expressed as

$$\kappa = \frac{uv}{\alpha}(1 - e^{-\alpha t}) , \tag{13}$$

where u is a factor which takes account of the compression of the impact instrument. Thus, from Eqs. (9) and (13), the triboluminescence intensity, that is, the rate of excitation of triboluminescence centers may be given by

$$I = \frac{dn}{dt} = \frac{\eta b V u^3 v^3}{\alpha^2 h^3} e^{-\alpha t}(1 - e^{-\alpha t})^2 \exp\left(-\frac{\beta u^2 v^2}{\alpha^2 h^2}(1 - e^{-\alpha t})^2\right) , \tag{14}$$

where h is the thickness of the crystal and $\epsilon = \kappa/h$.

For high values of the impact velocity, the time duration of triboluminescence is small and thus αt is much smaller than 1. Therefore, Eq. (14) may be written as

$$I = \frac{\eta b V u^3 v^3 t^2}{h^3} \exp\left(-\frac{\beta u^2 v^2 t^2}{h^2}\right) . \tag{15}$$

The similarity between the observed time dependence of triboluminescence empirically expressed by Eq. (1) and the derived expression given by Eq. (15) is consistent with the interpretation of the time dependence of triboluminescence in terms of the number and motion of mobile cracks. Equation (15) also explains the dependence of γ, the slope of the $\log(I/t^2)$ vs t^2 curve on the impact velocity and the thickness of the crystal, that is, $\gamma = \beta u^2 v^2/h^2$. This relation enables β to be determined from the slope of the $\log(I/t^2)$ vs t^2 curve.

B. Peak of the triboluminescence versus time curve

The differentiation of Eq. (14) shows that the triboluminescence intensity will be maximum when

$$2e^{-\alpha t} - (1 - e^{-\alpha t}) - \frac{2\beta u^2 v^2}{\alpha^2 h^2}(1 - e^{-\alpha t})^2 e^{-\alpha t} = 0 . \tag{16}$$

In the present investigation α is of the order of 10^3 and t is of the order of 10^{-4} sec. Hence αt is much smaller than 1. Thus the terms $(1 - e^{-\alpha t})$ in Eq. (16) can be neglected in comparison with $2e^{-\alpha t}$. However, the term $(1 - e^{-\alpha t})^2$ cannot be neglected as $2\beta u^2 v^2/\alpha^2 h^2$ is of the order of 10^2. Using this approximation, Eq. (16) becomes

$$e^{-\alpha t_m} = 1 - \frac{\alpha h}{\sqrt{\beta}\, uv} \tag{17a}$$

or

$$t_m = \frac{1}{\alpha}\ln(1 - \alpha h/\sqrt{\beta}\, uv)^{-1} . \tag{17b}$$

For smaller crystals and high impact velocities,

t_m may be expressed as

$$t_m = \frac{h}{\sqrt{\beta}\, uv}\,. \tag{18}$$

From Eqs. (14) and (17), the peak of the triboluminescence intensity may be expressed as

$$I_m = \frac{\eta b V u v}{\beta h e}\left(1 - \frac{\alpha h}{\sqrt{\beta}\, uv}\right),$$

or

$$I_m \approx \frac{\eta b V u v}{\beta h e}\exp(-\alpha h/\sqrt{\beta}\, uv) \tag{19}$$

for the smaller crystals and high impact velocities, where e is the base of the Neperian logarithm.

Figures 8(a) and 8(b) show that the plots of t_m vs $1/v$ and $\log(I_m/v)$ vs $1/v$ are linear in accord with Eqs. (18) and (19). The values of α and β are determined using the slopes of Figs. 8(a) and 8(b). This value of α is of the same order as that estimated from the logarithmic decrement of the compression rate at low value of the impact velocity, and the value of β is of the same order as that determined from the slope of $\log(I/t^2)$ vs t^2 curve. The values of α and β are given in Table I.

C. Total intensity of triboluminescence

The total intensity of triboluminescence may be given by

$$I_T = \int_0^\infty I\, dt\,.$$

By substituting the value of I from Eq. (14), I_T may be written as

$$I_T = \int_0^\infty \frac{\eta b V u^3 v^3 e^{-\alpha t}}{\alpha^2 h^3}(1 - e^{-\alpha t})^2 \times \exp\left(-\frac{\beta u^2 v^2 (1 - e^{-\alpha t})^2}{\alpha^2 h^2}\right) dt\,.$$

As $\alpha t < 1$, the above equation may be simplified as

$$I_T = \frac{\eta b V u^3 v^3}{h^3}\int_0^\infty \left(1 - \alpha t + \frac{\alpha^2 t^2}{2!} - \frac{\alpha^3 t^3}{3!}\right) t^2 \times \exp\left(-\frac{\beta u^2 v^2 t^2}{h^2}\right) dt$$

$$= \frac{\eta b V u^3 v^3}{h^3}\left(\frac{\sqrt{\pi}}{4}\frac{h^3}{\beta^{3/2} u^3 v^3} - \frac{\alpha h^4}{2\beta^2 u^4 v^4} + \frac{\alpha^2}{2!}\frac{3\sqrt{\pi}}{8}\frac{h^5}{\beta^{5/2} u^5 h^5} - \frac{\alpha^3}{3!}\frac{h^6}{\beta^3 u^6 v^6} + \cdots\right).$$

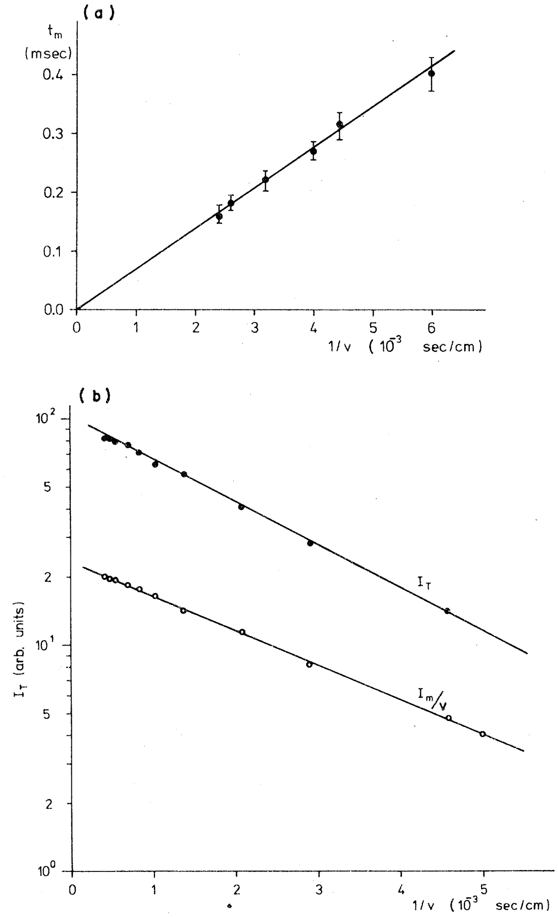

FIG. 8. Plots of (a) t_m vs $1/v$, (b) $\log(I_m/v)$ and $\log(I_T)$ vs $1/v$ for tartaric-acid crystals.

For smaller crystals and high impact velocities, the above equation may be written as

$$I_T \approx \frac{\sqrt{\pi}}{4}\frac{\eta b V}{\beta^{3/2}}\exp\left(-\frac{2}{\sqrt{\pi}}\frac{\alpha h}{\beta^{1/2} uv}\right). \tag{20}$$

Equation (20) explains both the increase of the total intensity of triboluminescence with increasing impact velocities[11,24] and its approach to a saturation value at high values of impact velocity. Figure 8(b) shows that the plot of $\log(I_T)$ vs $1/v$ is linear with a negative slope which supports Eq. (20). The value of $\alpha/\sqrt{\beta}$ determined from the plot 8(b) is of the same order as that calculated from the known values of α and β as determined above.

D. Dependence of triboluminescence on crystal size

Equation (19) suggests that at high impact velocities the dependence of the peak of the triboluminescence intensity versus time curve on the size of the crystals will be

$$I_{\max}=\frac{\eta buvA}{\beta e}, \qquad (21)$$

where $A=V/h$, the area of the crystal cross section. For a given high value of the impact velocity, the product of $I_{\max}$ and β is experimentally found to vary directly with the area of the cross section of the crystal, supporting Eq. (21).

Equation (20) shows the dependence of the total intensity of triboluminescence on crystal size. For high values of the impact velocities, Eq. (20) may be written as

$$I_T=\frac{\sqrt{\pi}\,\eta bV}{4\beta^{3/2}}. \qquad (22)$$

The product of I_T and $\beta^{3/2}$ is found to increase directly with the volume V or mass of the crystal. As β decreases with increasing size of the crystal, Eq. (22) suggests that the triboluminescence activity of a crystal should increase with increasing size of the crystal as was found in the earlier investigations.[3,8,25]

It follows from the above discussion that if two crystals of nearly the same dimensions were chosen and crushed with the same value of the high impact velocity, the peak in the triboluminescence intensity versus time curve in one of the crystals crushed along its longer side will be lower, and the time duration for the appearance of triboluminescence will be longer than that observed for a crystal crushed along a shorter side. The total integrated triboluminescence intensity will be the same in both the cases. These predictions are in accord with the experimental observations.

E. Physical significance of α and β

The parameter α was defined [Eq. (10)] as the rate constant of compression of the crystal. As a crystal is fractured its different parts begin to flow across each other and thereby the frictional force between the layers of crystal will oppose the rate of compression or the velocity of the piston. Thus α should be related to the crystal "viscosity" defined in this manner. Its value should increase with increasing viscosity and vice versa.

Equation (7) shows that β is a factor related to the decrease in the number of mobile cracks with the increase in the total number of cracks in the crystal. Hence in analogy with dislocation dynamics,[26] it should be a factor related to the attrition coefficient of the mobile cracks. Because the attrition coefficient will increase with increasing temperature, a decrease in triboluminescence activity with increasing temperature is expected, as has been reported for certain crystals.[2,16,27] A decrease in the normalization coefficient η is also expected with increasing temperature due to the changes in the physical properties of the crystals. Our preliminary results on the effect of temperature on the triboluminescence of crystals support the increase of β and the decrease of η. Detailed experiments are in progress.

F. Miscellaneous observations

Because triboluminescence occurs during the movement of cracks in crystals, the phenomenon may be useful in studies of fracture dynamics. The time duration of the triboluminescence pulse produced during the motion of a single crack is of the order of the time needed for the movement of a crack through the crystal. Thus, triboluminescence may provide a self-excited luminescence probe of the propagation of fracture and complement the techniques of defect photoluminescence where uv excitation can cause luminescence from defects formed at the onset of plastic deformation.[28,29]

The appearance of triboluminescence only during crystal fracture and its origin from excited N_2 suggest that a mechanism of excitation may involve creation of charged surfaces during the fracture followed by excitation of N_2 by electrons accelerated between the surfaces. Because all of the crystals studied in this paper are piezoelectric, the charging could be related to their piezoelectric behavior. However, the piezoelectric constants of the crystals[30-32] differ by less than a factor of 10 while the differences in triboluminescence intensity are on the order of 10^3 (Table I). Thus a direct connection between triboluminescence intensity and piezoelectric constant cannot be drawn. A second possibility that the triboluminescence intensity depends on the concentration of nitrogen in the crystal can also be ruled out. At atmospheric pressure newly created surfaces of a crystal become covered with an absorbed layer within about 10^{-7} to 10^{-8} sec.[33] The decay time of the triboluminescence from a single crack is longer, on the order of 10^{-5} to 10^{-6} sec. Thus it is likely that the amount of nitrogen contained in the crystal at the start of the experiment does not govern the triboluminescence intensity. Although the reasons for the varying triboluminescence intensities cannot yet be stated, the intensities will probably be related to the charge densities on the newly created surfaces which may differ from crystal to crystal due to the combined effects of different piezoelectric constants, charge leakages, direction of fracture propagation, and fracture stresses.

Luminescence probes of crystal deformation have been a subject of considerable interest.

The photoluminescence intensity of MgO, CaO, and SrO crystals and that of cathedoluminescence of MgO crystals depends on the density of defects produced during the deformation of the crystals.[28,29] In these crystals the defects produced during their deformation give rise to intrinsic luminescence centers. However, the triboluminescence in tartaric-acid, sugar, ammonium-tartrate, lithium-sulfate, and citric-acid crystals is not found during their deformation in the elastic and plastic regions. In addition, the triboluminescence in the crystals chosen in the present investigation is extrinsic, i.e., it occurs from N_2 molecules between the new surfaces created during fracture. Thus the triboluminescence gives a response to the formation of new surfaces or the movement of cracks in the crystals. Since a crack becomes mobile after a particular concentration of microscopic defects,[34,35] a relation may exist between the triboluminescence and the density of microscopic defects.

ACKNOWLEDGMENTS

One of the authors (B.P.C.) is grateful to the Ministry of Education and Social Welfare of the Government of India for the award of a national scholarship for post-doctoral research. The support of the Army Research Office, Durham and the Camille and Henry Dreyfus Teacher-Scholar-Award (J.I.Z.) are gratefully acknowledged. The authors also wish to thank Mr. Gordon E. Hardy for his help, Mr. Eric Olsen for designing and constructing the pneumatic instrument used to study the impact velocity dependence of triboluminescence, and Professor A. J. Ardell for making the Instron testing machine available.

---

*Permanent address: Department of Physics, Government College of Science, Raipur (M.P.) 492002, India.

[1] J. I. Zink, Acc. Chem. Res. 11, 289 (1978).

[2] A. J. Walton, Adv. Phys. 26, 887 (1977).

[3] A. Imhof, Phys. Z. 18, 78 (1917).

[4] W. G. Levison, Science 19, 826 (1904).

[5] G. Wolff, G. Gross, and I. N. Stranski, Z. Elektrochem. 56, 420 (1952).

[6] G. E. Hardy, J. C. Baldwin, J. I. Zink, W. C. Kaska, P. H. Liu, and L. Dubois, J. Am. Chem. Soc. 99, 3352 (1977).

[7] D. M. Nelson, J. Opt. Soc. Am. 12, 207 (1926).

[8] F. G. Wick, J. Opt. Soc. Am. 27, 275 (1937).

[9] B. P. Chandra, N. Periasamy, and J. N. Das, Pramana 8, 395 (1977).

[10] B. P. Chandra, Indian J. Pure Appl. Phys. 14, 874 (1976).

[11] B. P. Chandra and K. K. Shrivastava, J. Phys. Chem. Solids 39, 939 (1978).

[12] J. N. Das, B. P. Chandra, and P. R. Tutakne, Phys. Status Solidi A 11, K59 (1972).

[13] L. Sodomka, Czech. J. Phys. B24, 469 (1974).

[14] I. Chudacek, Czech. J. Phys. B16, 520 (1966).

[15] K. Meyer, D. Obrikat, and M. Rossberg, Krist. Tech. 5, 5 (1970); 5, 181 (1970).

[16] F. Fröhlich and P. Seifert, Cryst. Lattice Defects 2, 239 (1971).

[17] G. Alzetta, I. Chudacek, and R. Scarmozzini, Phys. Status Solidi A 1, 775 (1970).

[18] B. P. Chandra and M. Elyas, Krist. Tech. 11, 1341 (1978).

[19] G. E. Hardy and J. I. Zink, Inorg. Chem. 15, 3061 (1976).

[20] G. Herzberg, *Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules* (Van Nostrand, Princeton, 1950), 2nd ed., p. 324.

[21] W. A. Wooster, *Textbook on Crystal Physics* (The University Press, Cambridge, 1938), p. 53.

[22] F. Seitz, Rev. Mod. Phys. 18, 384 (1946).

[23] W. G. Knauss, in *Proceedings of the First International Conference on Fracture, Sendai, Japan, 1965* (Japanese Society for Strength and Fracture of Materials, 1966), p. 1139.

[24] B. P. Chandra and M. Elyas, Indian J. Pure Appl. Phys. 15, 744 (1977).

[25] B. P. Chandra and P. R. Tutakne, Indian J. Pure Appl. Phys. 16, 688 (1978).

[26] J. J. Gilman, *Micromechanics of Flow of Solids* (McGraw-Hill, New York, 1969), p. 195.

[27] J. N. Das and B. P. Chandra, Phys. Rev. B 10, 3518 (1974).

[28] Y. Chen, M. M. Abraham, T. S. Turner, and C. M. Nelson, Philos. Mag. 32, 99 (1975).

[29] M. A. Velednitskaya, V. N. Rozhanskii, L. F. Comolova, G. V. Saparin, J. Schreiber, and O. Brümmer, Phys. Status Solidi A 32, 123 (1975).

[30] W. F. Hoiman, Ann. Phys. (Leipzig) 29, 160 (1909).

[31] W. P. Mason, *Piezoelectric Crystals and Their Application to Ultrasonics* (Van Nostrand, Princeton, 1950), p. 229.

[32] F. Spitzer, Electr. Commun. 28, 300 (1951).

[33] V. Ponec, Z. Knor, and S. Cerny, *Adsorption on Solids* (Chemical Rubber Co., Ohio, 1974), p. 19.

[34] H. G. Van Bueren, *Imperfections in Crystals* (North-Holland, Amsterdam, 1968), p. 492.

[35] J. Friedel, *Dislocations* (Pergamon, New York, 1964), p. 328.