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Sonoluminescence in granular media

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We report an experimental observation of sonoluminescence (SL) from ZnS:Mn and ZnS granular mixtures. The mechanism of SL is suggested to arise from a grain collision-induced excitation of electrons and holes recombining through defect states located in the near surface regions of the grains. Pressure-induced broadening and thermal phenomenon are likely involved in producing broad emission bands of observed SL. A heterogeneous spatial distribution of SL is suggestive of a grain aggregation at acoustic driving. A simplified description of grain movements in the framework of continuum mechanics approach yields an accurate account of the observations. The SL phenomenon may be useful in gaining insight into the dynamical behavior of granular media. [S0163-1829(97)00446-3]

The luminescence from the sound field in a liquid known as sonoluminescence (SL) has been of interest for many years.[1] The sonoluminescence does not result from the sound directly but arises through a cavitation process. The appropriate effect in solids has come to be known as acoustoluminescence.[2] The light production occurs via a movement of dislocations.[2,3] In both cases, however, the emission process is made up of a complex effect governed by either bubble or dislocation dynamics. Towards this end, granular material appears to exhibit not only solidlike but also fluidlike behavior resulting in exceptional properties and, particularly, in unusual dynamics.[4] This work is focused on the observation of the sound-induced light emission from a granular medium. Also at issue here is an exploration of the possible connections of sonoluminescence and the dynamics of a granular mixture subjected to acoustic driving.

A ZnS:Mn (0.5 wt. %) powder of 99.999% purity and a nominally pure ZnS powder (99.99%) obtained from the Furuuchi Chemical Company with grains of various shapes have been used as a model for granular matter. The linear dimensions of the grain differed no more than by a factor of 1.5–1.6 and were centered at about 3 μm. Powder 1 was contained in a 6-mm-diam. and about a 1-mm-deep cylindrical glass-walled flask 2 with a glass plate end cap 3, as shown in the upper inset of Fig. 1. It was slightly compressed by covering it with a Y-cut 550-μm-thick $LiNbO_3$ piezoelectric plate 4 which drives acoustic waves propagated along the z axis of a lithium niobate. In our experiments, Lamb waves were excited by applying rf voltage U to the silver electrodes 5. We tested the existence of the waves by using two pairs of electrodes deposited on both sides of a $LiNbO_3$ plate and rf pulse driving. The output signal was found to be linear over the applied voltage range. We can launch the lowest-mode Lamb waves used in the frequency range from 1 to 6 MHz. In SL measurements, the frequency of applied voltage was tuned in order to achieve maximum SL signal such that the data presented here were taken at a frequency of about 3.4 MHz. So far, we have no means reliably relating the network of forces within the granular material 1 to the external forces impressed by a driving plate, implying the plate waves are of a complicated mixed character with both the longitudinal and transverse displacements.[5] The voltage U is used as a measure of external driving force. The cell was vertically oriented and closed with a screen 6 separated by a gap width of approximately 0.5 mm from a $LiNbO_3$ plate. A screen hole was positioned to view the cell, as marked by the dashed lines in the inset. To test gravity effect the cell was tilted in the base plane such that a sound in a $LiNbO_3$ plate propagates along the axis which is about 25° away from the vertical direction. A powder sonoluminescence light transmitted by a transparent $LiNbO_3$ plate was focused onto an intensified 576 G/RB CCD camera (Princeton Instruments) connected to a computer. The image of the 6 mm gap spanned 341 pixels. The image detection system was found to be linear over at least two orders of magnitude change of photon flux. Care was exercised to ensure emission intensity changes to be within this linear range. Photoluminescence (PL) was taken with a 325 nm line of a He-Cd laser. Luminescence spectra were analyzed using a Spectra Pro-150 (Acton Research) monochromator with 300 g/mm grating and the same CCD camera. Overlapping data sets were taken in order to cover the entire spectral range extending from 300 to 900 nm. The detection system was calibrated over the

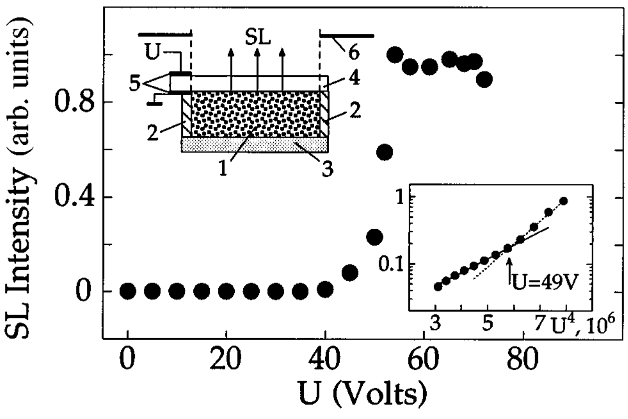

FIG. 1. Dependence of the total SL intensity from a ZnS:Mn mixture in the attainable spectral range on applied voltage U amplitude. Upper inset: schematic of the side view of the ultrasonic setup (see text for details); the dimension of electrodes 5 is about $5\times0.5\ \mathrm{mm}^2$. Lower inset: dependence of $\ln I$ vs U^4 as discussed in the text.

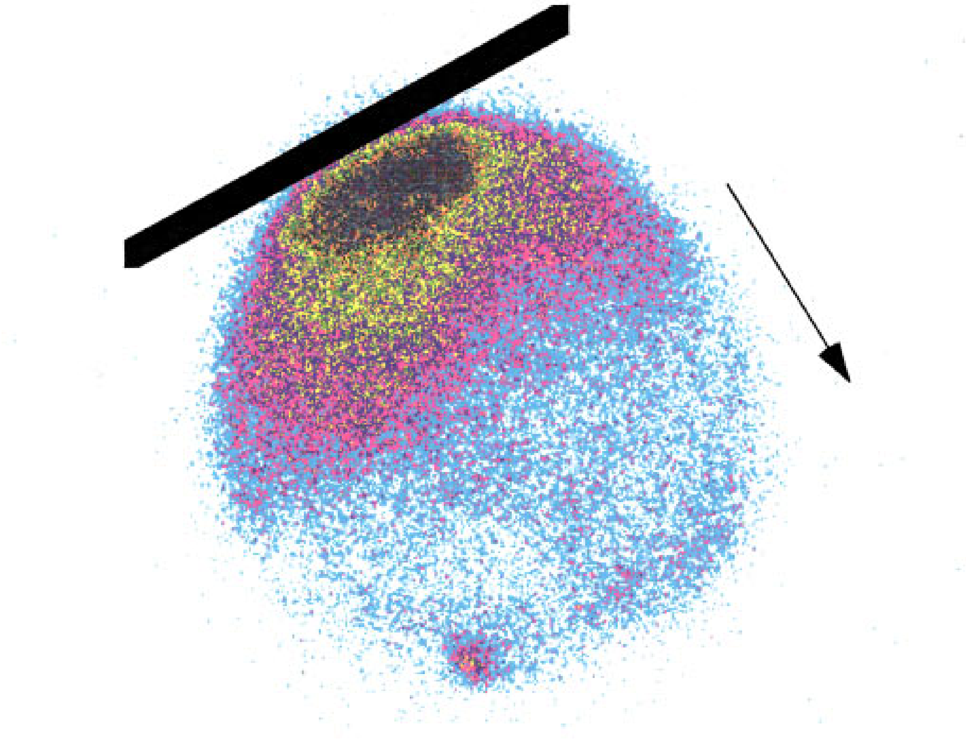

FIG. 2. (Color) CCD image of ZnS:Mn SL taken at $U=68$ V. The color scheme is black →yellow→magenta→green→blue →white for maximum to minimum SL intensity. The dark stripe shows an orientation of the exciting electrode while the arrow indicates the sound wave propagation direction in a $LiNbO_3$ plate.

entire range against a tungsten standard lamp. The SL data were not corrected for the transmission of light through a $LiNbO_3$ plate of the cell. All the experiments were performed at room temperature.

Upon a certain threshold value of U (about 40 V in our measurements), sonoluminescence from a ZnS:Mn powder appears. Its intensity is weak but SL is bright enough to be visible with the lights off in the lab. Figure 1 displays representative SL intensity vs U. SL from ZnS powder also was observed but of very low intensity. Hence, we note that conversion of acoustic energy into light occurs; the question is why. Two effects seem potentially relevant: (1) electroluminescence (EL) of a powder in electric fields accompanying acoustic waves in a piezoelectric $LiNbO_3$. We emphasize that such an effect is reminiscent of that governing observed ''acousto-electroluminescence'' phenomena;[6] (2) inelastic particle collisions in a dissipative granular medium at acoustic driving. Clearly, any one or combination of the electric field-, deformation-, and thermally induced luminescence phenomena could be capable of describing SL production in the mechanism (2).

For an understanding of the light production, we implemented a two-dimensional visualization of SL. A typical SL image taken from a ZnS:Mn material is shown in Fig. 2. Most notably, SL appears to be very heterogeneous. The picture is quite different from what is expected by the mechanism (1) since the electroluminescence image in the piezoelectric fields of acoustic waves has generally tended to exhibit an equidistant spatial profile.[6] In contrast, the observed image bears resemblance to that which can be thought of as a map of the regions with increased packing density of grains, due to the movements of powder particles induced by the acoustic wave. We note that both to-and-fro motions and tangential boundary viscosity streaming can be produced by a harmonically varying movement of a sound source.[7] Particularly, the transport of powdered granular solids has been observed at Lamb wave driving.[8]

To test this suggestion, the ZnS:Mn powder was poured between a $LiNbO_3$ plate and an opposing glass plate separated by ≈ 200 μm. The cross section of this setup is similar to that presented in the upper inset of Fig. 1. However, no bounded wall 2 was introduced in this measurement. Most notably, it was found that there occurs a break in the powder uniformity at driving voltages as high as 55 V. Interestingly, a jump in the SL intensity occurs roughly at the same driving, as evidenced in Fig. 1.

Taken together, the above observations are consistent with the grain collision-induced mechanism (2) of SL. Indeed, the driving on a MHz frequency scale is characterized by the typical mean amplitude ($\sim 10^{-8}$ m), considerably less than the grain diameter ($\sim 10^{-6}$ m), such that a mixture of horizontal and vertical displacements of the driving plate likely produces a random velocity field for the grains near the plate. An analog of the energy transfer mechanism in the molecular system interacting with a wall is therefore anticipated. The near plate disturbances are damped in the interior of the mixture by grain collisions. It is worthwhile to emphasize that these collisions are inevitably inelastic and not central, so that frictional forces are exerted. Hence, increased pressures, induced electric fields, and localized heating of rubbing particle surfaces are possible candidates for the explanation of the light observed in sonoluminescence. These factors are likely to initially enhance SL at $U \leqslant 50$ V. Mention must also be made that at this low driving level, the SL image has been found to be not nearly as heterogeneous as that in Fig. 2. Assuming the above excitation model to be the case, the grain surface state would be a key physical parameter for the SL phenomenon. As the impact velocity is increased further, more energy goes into irreversible work in the contact region. This has led us to consider a number of powders obtained from different laboratories, both undoped and doped with Mn and Cu impurities. There appears to be no obvious correspondence between PL efficiency and SL intensity of the powders. Therefore, doping itself does not play a demonstrably important role in SL appearance but would probably affect the surface of the grains.

In order to treat the model quantitatively, let v be the average velocity of a grain near the driving wall, ξ the average spacing between nearest grains, m and $2r$ the mass and diameter of the grains, respectively, which are assumed to be identical. Following the molecular kinetic approach,[9] the pressure exerted by the driving plate can be simply expressed as $p \propto \Delta K/\tau(2r)^2$, where $\Delta K \propto mv$ is the momentum transfer in a collision of two grains and $\tau \propto \xi/v$ is the grain collision time. Hence, for the given grain mixture the pressure becomes $p \propto v^2/\xi$. Here we approximate the average grain velocity near the driving surface by assuming $v \propto \omega A \propto U$ with A the amplitude of surface motion and ω the frequency of the ultrasonic wave. Finally we find $p \propto U^2/\xi$. To proceed further, underlying assumptions concerning the energy transfer from initial mechanical disturbances into light must be complemented. To overcome this rather complicated problem and to make a crude approximation, we implicitly take the logarithm of emission intensity I to be proportional to p^2 originating with Alzetta, Minnaja, and Santucci[10] for pressure-induced luminescence of ZnS phosphors. Accordingly, we then equate

$$\ln I \propto U^4/\xi^2. \tag{1}$$

In order to check this dependence, detailed data taken for the region of SL increase are plotted in the lower inset in Fig. 1. Examining them, it is pleasing to conclude that the model which is still crude nevertheless gives an accurate account of the observations. First, two distinct regions which agree fairly well with Eq. (1) are clearly seen. Second, a pronounced bend of the curve marked by the arrow appears upon the increase of U. The slope increase observed at $U \geqslant 49$ V would imply the decrease of the intergrain separation ξ in accordance with Eq. (1). This in turn might suggest that the SL-intensity jump at about 50 V in Fig. 1 originates from the regions of closely packed grains and this fact is consistent with the observation of a heterogeneous image in Fig. 2. In this respect, we assign the regions of intense SL (black dots in the upper part of Fig. 2) to the formation of grain aggregates at acoustic driving and subsequently an enhanced collision rate (proportional to ξ^{-1}) of powder particles within such aggregates. Within the aggregates, the average velocity of the particles is expected to considerably decrease. We therefore expect that SL would rise quite abruptly and then exhibit a very slow increase or even settle down at some level of intensity. Figure 1 clearly indicates that this is the case experimentally. It must be pointed out that such a behavior obviously is at variance with the electroluminescence (1) hypothesis. Also of note is that the region of intense SL (black dots in Fig. 2) is about 1 mm away from the edge of exciting electrodes. This observation is qualitatively consistent with the model of particle transport along the sound direction. Indeed, as already mentioned, the harmonic plate motions exert steady viscous stress on the boundary. As a consequence, it seems to be not unreasonable to expect increased packing density at the finite distance away from the sound source since there is no continuous removal of adhering surface layers in a dense grain mixture. This effect has been found to be a rather universal behavior. Meanwhile, the SL intensity distribution behind this region along the wave axis varied in repeated measurements with newly packed mixtures of grains. A series of measurements has produced SL profiles with additional peaks of lower intensity as exemplified in Fig. 3.

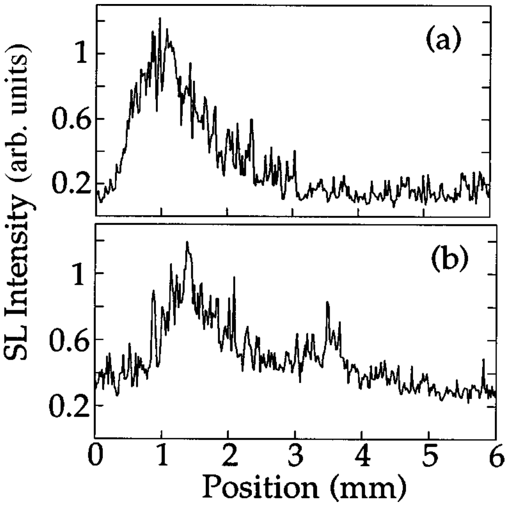

FIG. 3. Examples of SL intensity cross sections across the wave axis for different grain packing. The plot (a) is a middle profile of the image in Fig. 2. Both the (a) and (b) plots are normalized to their maxima.

We also emphasize that the picture in Fig. 2 is asymmetric relative to the sound propagation direction and is slightly expanded along the vertical axis. Additionally, a small region of increased SL appears to be just at the bottom of the cell. By taking into account the possibility of the gravity mediated packing of a granular material in the vertical direction due to vibrations in the sound field, the latter two facts might initially be expected in the proposed model. As another check of the reliability of our analysis, we excited a ZnS:Mn granular mixture with the lowest eigenmode of the thickness vibrations of a $LiNbO_3$ plate utilized by covering the surfaces of the plate by thin, semitransparent gold layers. Resulting SL was imaged in the central part of Fig. 2 and, again, was slightly expanded in the vertical direction.

In justification of our model, we also attempted to evaluate the suggested variation of packing density by attributing the change in the slope of the fits in the lower inset in Fig. 1 to the change of the intergrain separation ξ. The packing density, $\eta = (\frac{4}{3})\pi r^3/$(volume per grain in a mixture), for the spherical particles has been found to fall in a range from $\eta \approx 0.56$ in the lower limit of random loose packing to $\eta \approx 0.64$ for the upper limit of random close packing.[11] If we take the volume per grain in a mixture to be $\approx (\frac{4}{3})\pi(r + \xi/2)^3$ and assume initially loose packed density with $\eta = 0.56$, the increase in the slope at $U \geqslant 49$ V in the lower inset in Fig. 1 can be easily related to the decrease in the intergrain separation from $\xi \approx 0.64$ μm to $\xi \approx 0.49$ μm. This readily gives $\eta \approx 0.63$ for the close packing regions in Fig. 2.

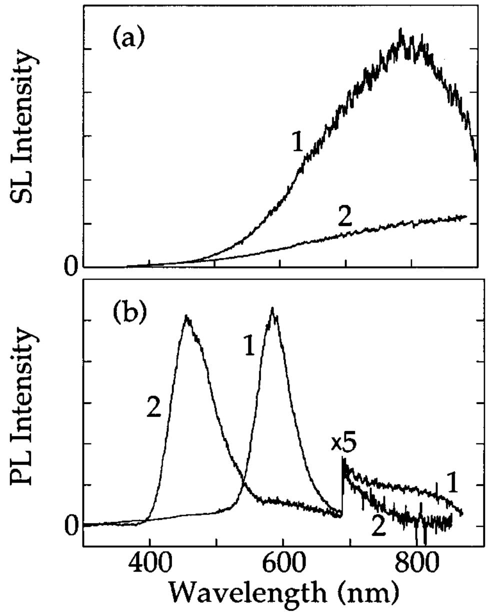

FIG. 4. Comparison of the spectra of SL (a) and PL (b) from ZnS:Mn (1) and ZnS (2) mixtures. The SL spectra are taken at $U = 68$ V and match in the low-wavelength region while total image computed SL intensities from ZnS:Mn and ZnS mixtures are in the ratio 1:0.19. The PL spectra are normalized to their peak height.

The reasonable value obtained is illustrative of the satisfactory way in which SL excitation is ascribed to the grain dynamics.

To explore the luminescence centers involved, the spectral analysis of SL was employed. Figure 4 displays the spectra of SL (a) and PL (b) of the grain mixtures. The key features are apparent in the plots: first, the broadband nature of SL [spectra 1 and 2 in Fig. 4(a)], and second, the prominent PL bands of the Mn^{2+} ion yellow emission[12] at around 585 nm in ZnS:Mn [spectrum 1 in Fig. 4(b)] and blue self-activated emission at about 450 nm in pure ZnS related to the zinc vacancy center[13] [spectrum 2 in Fig. 4(b)] are undetectable in the SL spectra. It is by no means certain that SL is not accomplished by the same luminescent centers responsible for PL. This fact also impedes ascribing SL to the electroluminescence mechanism (1) since EL spectra of ZnS:Mn phosphors are known to generally coincide with those of PL.[14] Since the Mn^{2+} d-electron states are known to act as effective luminescence centers, it seems unlikely that SL originates in the interior of the grains. The near surface origin of observed SL can therefore be suggested, as already pointed out. It should be noted that highly doped ZnS:Mn crystals have been found to exhibit an emission band at around 800 nm,[15] tentatively ascribed to optical transitions with intrinsic defects although the nature of the defects is not definitely known. It is seen in Fig. 4(b) that similar band can be distinguished on the long-wavelength side of the Mn^{2+} emission tail (spectrum 1) whereas almost no emission of undoped grains has been detected in this region (spectrum 2). In accord, the SL spectrum of ZnS:Mn [1 in Fig. 4(a)] displays a pronounced emission peak near 800 nm while there appears to be no obvious peaks in the spectrum of undoped ZnS [2 in Fig. 4(a)]. Closer examination of the latter spectrum, however, discerns a weak band in the spectral range from 600 nm to about 850 nm. The PL spectrum of undoped grains [2 in Fig. 4(b)] also shows evidence of a subsidiary emission above 570 nm, so that a defect participation in SL of undoped grains [spectrum 2 in Fig. 4(a)] could also be implied. As regards the broadband spectra of SL presented in Fig. 4(a), the pressure-induced broadening and the thermal phenomenon can presumably be viable explanations.

In conclusion, we have presented an experimental observation of sonoluminescence from ZnS:Mn and ZnS granular mixtures. On the basis of the experimental evidence there is strong reason to term this phenomenon as the grain collision-induced light emission. Electrons and holes excited in the impacts are hypothesized to recombine through defect states predominantly located in the near surface region of the grains. The simplified molecular kinetic approach within the framework of continuum mechanics can serve at best as a crude approximation to the dynamics of a granular mixture subjected to a MHz frequency oscillating motion. A highly heterogeneous spatial distribution of SL is suggested to be a manifestation of the formation of grain aggregates at acoustic driving. Sonoluminescence can thus be linked as a means of access to the dynamic properties of granular media.

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