Spectral dependence of the acoustic properties of proustite close to the 210 K phase transition

1992 J. Phys.: Condens. Matter 4 L51

(http://iopscience.iop.org/0953-8984/4/3/001)

J. Phys.: Condens. Matter 4 (1992) L51–L54. Printed in the UK

LETTER TO THE EDITOR

Spectral dependence of the acoustic properties of proustite close to the 210 K phase transition

Xiaoli Zhao†, J I Dunlop and K N R Taylor
Advanced Electronic Materials Group, Department of Applied Physics, University of New South Wales, Post Office Box 1, Kensington, NSW, 2033, Australia

Received 23 August 1991

Abstract. Experimental results are presented for the ultrasonic velocity and attenuation of shear waves at 2.4 MHz in proustite. The effects of the polarization and wavelength of irradiation in the range 450–900 nm on the photoinduced phase transition at 210 K are reported.

The properties of crystalline proustite ($Ag_3A_3S_3$) are known to be affected by irradiation with white light, and in particular there is considerable evidence [1–5] for an optically induced phase change close to 210 K. While some workers [6, 7] have failed to observe changes that can be associated with such a transition, it is clear that the transition is accompanied by significant effects in observations of the phonon spectra [1], dielectric properties [2, 3] and optical absorption [4, 5].

We have also recently reported [8] that the ultrasonic attenuation of proustite is significantly enhanced by exposure to white light in a small temperature range near to 210 K, and believe that this too is associated with changes in the structural order associated with the phase change. We have now extended this research to include measurements of the velocity and attenuation of both dilatational and shear waves, and the effects of wavelength and plane of polarization of the irradiating light. The results of these measurements are described in the following.

Two samples were used in these experiments, one in the form of a rectangular prism with dimensions of $8.8 \times 8.5 \times 9.8$ mm^3 cut along the crystallographic a, b and c axes, and the other in the shape of a cylinder of length 20 mm parallel to the a axis and of diameter 10.3 mm.

A dilatational ultrasonic transducer of resonant frequency 5.2 MHz and shear wave transducer of frequency 2.4 MHz, together with conventional pulse-echo equipment, were used in these experiments. At room temperature, the velocity of dilatational waves along the c axis was measured as 2700 ± 20 m s^{-1}, in agreement with previous reports [9]. However, along the a and b axes, the measured velocity was 3000 ± 30 m s^{-1}, much higher than along the symmetry axis c. Shear wave velocities were measured as 1230 ± 20 and 1470 ± 20 m s^{-1} along the a axis with particle displacements along the b and c axes,

† On leave from: Applied Acoustics Institute, Shaanxi Teachers University, Xian, People's Republic of China.

0953-8984/92/030051 + 04 $03.50

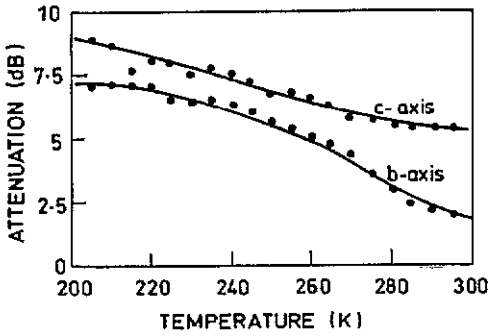

Figure 1. The attenuation of shear ultrasonic waves of 2.4 MHz in the rectangular single crystal of proustite along the *a* axis, as a function of temperature. The different curves relate to particle displacements along the *b* and *c* axes respectively.

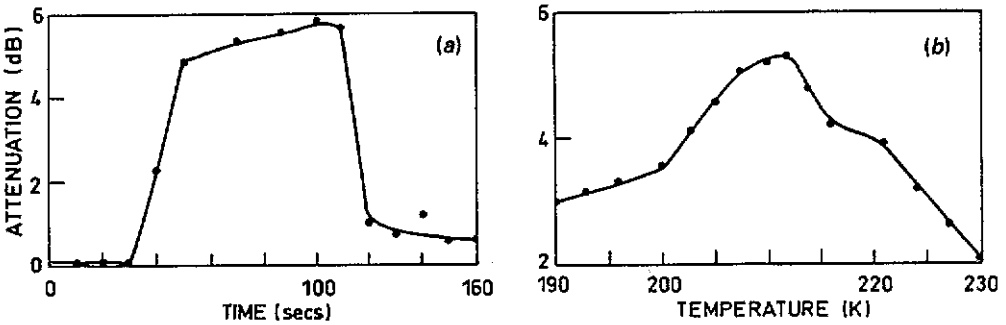

Figure 2. (*a*) Changes in the shear wave attenuation at 2.4 MHz parallel to the *a* axis and with particle displacement along the *b* axis, resulting from exposure to light along the *b* axis, at 210 K. The illumination was switched on at 30 s and off at 110 s. (*b*) The variation of the magnitude of the optically induced change in attenuation at 2.4 MHz with temperature from 190 to 230 K for shear waves travelling along the *a* axis, particle displacement along the *b* axis, and light incident along the *c* axis of the rectangular crystal.

respectively. No other satisfactory shear wave measurements were possible with the samples used.

Shear waves of 2.4 MHz were launched into the unilluminated proustite sample at cryogenic temperatures (the dark condition) and figure 1 shows the temperature dependence of the attenuation, for shear waves propagating along the *a* axis, for particle displacements parallel to the *b* and *c* directions. The observed attenuation constant is similar to that measured for dilatational waves.

The influence of light on the attenuation of shear waves travelling in the *a* direction, near to 210 K has also been measured. The results are similar to, but more significant than those observed in our previous experiments for dilatational waves. The observed enhancement of the attenuation for both types of wave near 210 K is shown in figure 2. Corresponding to these changes in the attenuation during illumination of the samples, we also find that the velocities of both dilatational and shear waves undergo a very small ($\simeq 0.01\%$) but significant decrease.

During some of the observations a polarizer was inserted into the light path and rotated through 360° during both dilatational and shear wave measurements. No variation was found in the attenuation during this process, suggesting that the photoinduced process is not closely related to the structure of proustite.

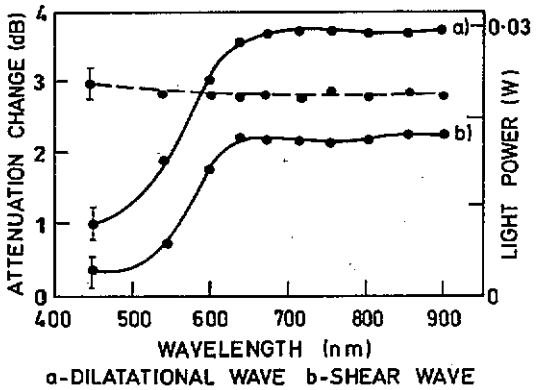

Figure 3. The power of the light passed by each of the ten filters of bandwidth 10 nm and of different central wavelengths ranging from 450 nm to 890 nm (dotted curve), and changes in the attenuation of dilatational (5.2 MHz) and shear (2.4 MHz) waves for various wavelengths of the illuminating light (incident along the c axis of the cylindrical sample). Typical error bars are shown.

Since we believe that we are observing some kind of photoexcitation process the ultrasonic attenuation in the proustite sample was measured at 210 K as a function of the wavelength of the illuminating light. In order to do this, light from a conventional slide projector was focused onto an area of the sample of diameter 2 mm through a series of optical interference filters of bandwidth 10 nm and with different central wavelengths within the range 450–900 nm. To ensure that any observed effects were not associated with the filter transmittance, the light power was measured at the sample position for each of the filters and as shown in figure 3 this is essentially constant over the wavelength range studied. The observed enhancement of the ultrasonic attenuation of dilatational waves as a function of the wavelength shows a clear cut-off in the region between 500 and 600 nm, as may be seen in figure 3, with the photoinduced change increasing markedly at higher wavelengths. The value of this cut-off wavelength agrees with the reported absorption edge in the optical spectrum of proustite between 400 and 650 nm [4]. The same wavelength effect was observed with shear wave measurements as also shown in figure 3.

While the wavelength of the cut-off in the attenuation enhancement is close to the absorption edge, it must be stressed that the photoinduced effect occurs on the long-wavelength side of this edge, i.e. at lower photon energies. This is in marked contrast to the normal behaviour in photoexcitation processes.

It is generally accepted that the observed transition is driven by the redistribution of silver ions between the various possible silver sites in the lattice under the influence of the illumination. It is clear then that during the dynamic redistribution process the attenuation enhancement is significantly lower for the higher-energy photons of wavelength below the absorption edge than it is for the lower-energy photons ($\lambda > 600$ nm).

A number of possible mechanisms can be considered to account for these observations, all of which rely on the differences in the ultrasonic scattering between a disordered array of Ag^+ ions in lattice sites and a liquid-like 'sea' of photoexcited silver ions, being continuously redistributed between sites. The long relaxation times of the dielectric behaviour ($\simeq 10^3$ s) suggest that these photoinduced effects are likely to be closely linked to a thermal redistribution of the disordered Ag^+ ions. In the present measurements, however, the relaxation times for the changes in ultrasonic attenuation are only of the order of a few seconds. While this might appear to suggest the association of the enhanced attenuation with the photoexcited silver ions it is likely, however, that

the mean free time that the ions spend between sites during the hopping motion will be too small to have a significant effect on the propagating ultrasonic wave.

A simpler interpretation of the observed effects is that the band edge for Ag^+ ion excitation lies beyond 900 nm and that the observed cut-off close to 600 nm is the immediate consequence of the decreased penetration of the higher-energy photons into the body of the sample. For wavelengths less than 600 nm, the high optical absorption coefficient will restrict the observable effects to the surface regions, while above 600 nm any photostimulated changes will be sensed by the ultrasonic pulses provided that the activation energy for the process is less than approximately 1 eV corresponding to an absorption edge beyond $\lambda \simeq 900$ nm, the long-wavelength limit of this work. This is clearly consistent with the present observations and it is necessary to extend the present observations to infrared wavelengths. This relatively small activation energy would be consistent with the observation of thermally assisted hopping at 210 K and with the lack of an observable direct absorption edge at wavelengths less than 1 μm [3].

References

[1] Smolenskii G A, Sinii I G, Kuzminov E V and Godovikov A A 1979 *Sov. Phys.–Crystallogr.* **21** 1343
[2] Yang S R and Taylor K N R 1991 *Phys. Rev.* B submitted
[3] Yang S R, Taylor K N R and Zhang F Y 1989 *J. Phys.: Condens. Matter* **1** 1663
[4] Yang S R and Taylor K N R 1986 *Solid State* **29** 1459
[5] Taylor K N R and Yang S R 1989 *Solid State Commun.* **71** 619
[6] Ewen P J S, Taylor W and Paul G P 1983 *J. Phys. C: Solid State Phys.* **16** 6475
[7] Nelmes R J, Howard C J, Ryan T W, David W I F, Schultz A J and Leving P C W 1984 *J. Phys. C: Solid State Phys.* **17** L861
[8] Dunlop J I, Taylor K N R and Zhao Xiaoli 1991 *J. Phys.: Condens. Matter* **3** 4753
[9] Gorin Yu F, Kobelev S, Babushkin A N and Kuznetsov Yu S 1983 *Sov. Phys.–Solid State* **25** 531