

Temperature and pressure dependence of the elastic properties of RbAg_4I_5

L. J. Graham and R. Chang

Science Center, Rockwell International, Thousand Oaks, California 91360
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An ultrasonic pulse superposition technique was used to measure the velocities of the three pure-mode waves which propagate along [110] in a single crystal of rubidium tetra-silver pentaiodide. The temperature was varied from 25 °C, through a phase transformation at -65 °C, and to a second phase transformation at -151 °C. There was a peak in the ultrasonic attenuation at the -65 °C transition for the longitudinal and one of the shear waves, and the attenuation and velocity of all of the waves were completely reversible upon cycling the temperature through this transition. The lower-temperature phase was generally several percent softer elastically than the room-temperature phase. Attempts to make measurements through the -151 °C transition were not successful. The pressure dependence of the wave velocities were determined at 25 °C. The adiabatic second-order elastic constants and their temperature and pressure derivatives at 25 °C which were determined from these measurements are as follows. The values of C_{ij} (10^{11} dyn/cm²), $C_{ij}^{-1} (\partial C_{ij} / \partial T)$ (10^{-4} °K⁻¹), and $\partial C_{ij} / \partial P$ for C_{11} are 1.648 ± 0.002 , -3.54 ± 0.12 , and $+8.73 \pm 0.11$, respectively; for C_{12} , 0.934 ± 0.002 , -3.73 ± 0.13 , and $+6.29 \pm 0.11$, respectively; and for C_{44} , 0.4892 ± 0.0005 , -4.17 ± 0.05 , and $+0.884 \pm 0.015$, respectively. The Debye temperature of 90 °K and the thermal expansion coefficient of 0.566×10^{-4} °K⁻¹ calculated from these values agree very well with values determined by other means.

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I. INTRODUCTION

Rubidium tetra-silver pentaiodide is a member of the isostructural group of ionic compounds with the composition $M\text{Ag}_4\text{I}_5$, where M includes Rb, K, and NH_4 .¹⁻³ These compounds have the highest electrical conductivities of any known ionic solids, comparable to those of liquid electrolytes at room temperature. They are all thermodynamically unstable below room temperature, but can be retained for indefinite periods in a dry atmosphere well below room temperature. Of the three, the rubidium salt is the most stable and is of the greatest practical interest. During the five-year period, 1970 through 1974, over 50 research papers were published and 30 patents filed concerning this material. The present paper reports the only known measurements of its elastic properties, however. In this paper we report the results of measurements of the ultrasonic wave velocities and attenuation below room temperature, through a phase transformation at -65 °C, and to a second phase transformation at -151 °C. Also reported are the pressure dependences of the ultrasonic wave velocities at 25 °C. From these measurements the second-order adiabatic elastic constants and their temperature and pressure derivatives at 25 °C were calculated. Other parameters such as the Debye temperature, thermal expansion coefficient, and equivalent isotropic elastic moduli which can be calculated from the single-crystal elastic constants are also reported.

II. EXPERIMENTAL PROCEDURE

The elastic constants of RbAg_4I_5 were measured using a sensitive phase-comparison ultrasonic pulse-echo method⁴ on a single crystal grown using the Czochralski technique.⁵ At room temperature this material has a cubic crystal structure⁶ and thus its elastic

properties are described by three independent elastic constants C_{11} , C_{12} , and C_{44} . These can be determined conveniently by measuring the three independent ultrasonic wave velocities which can propagate along a [110] direction in the crystal and which provide three combinations of the elastic constants as the product of the velocity squared times the density. These three velocities were measured as a function of temperature at 1 atm pressure and as a function of pressure at 25 °C. During the temperature runs, the ultrasonic attenuation was also monitored.

The size of the single crystal used in this study was $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{8}$ in., oriented so the $\frac{1}{8}$ -in. direction through the crystal was the [110] wave propagation direction. The two $\frac{1}{2}$ -in. square {110} faces were polished optically flat and parallel. The ultrasonic measurements were made using $\frac{1}{8}$ -in.-diam 16-MHz quartz transducers bonded to the [110] face with Salol between room-temperature and about -45 °C, and with 2.5×10^6 -centistoke Dow Corning 200 silicone fluid below -45 °C. The x-ray density of $\rho = 5.384$ g/cm³ determined by Geller⁶ was used in calculating the elastic constants.

III. PHASE TRANSFORMATIONS IN RbAg_4I_5

RbAg_4I_5 undergoes two phase transformations below room temperature, at about -65 °C and -151 °C. Upon cooling a single crystal below -65 °C it becomes optically birefringent; this transition is reversible with no hysteresis.⁶ At this temperature there is only a slight change in slope of the temperature dependence of electrical conductivity,¹ and the x-ray powder pattern at -100 °C shows line broadening and at least one split line.⁶ Although the crystal structure of this intermediate phase has not been determined it cannot be cubic, and therefore more than three elastic constants are required to describe its elastic behavior. However, the

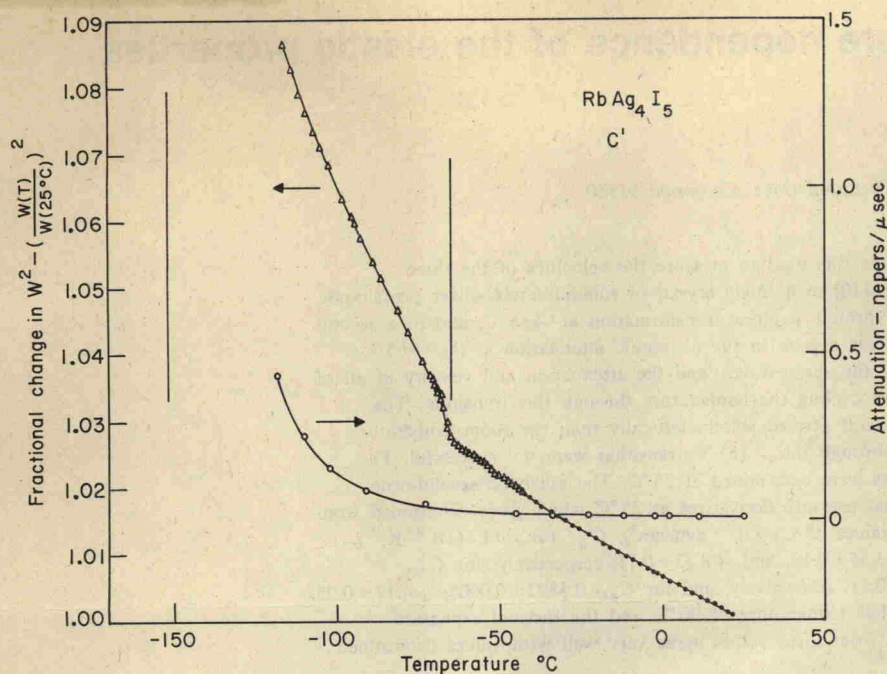


FIG. 1. Data for the shear mode which determines the C' elastic constant. Phase transformations occur at -65 and -151 $^{\circ}\text{C}$.

ultrasonic pulse-echo patterns observed below the -65 $^{\circ}\text{C}$ transition showed no detectable distortion. This can only be explained if the wave propagation direction happened to be a pure-mode direction in the noncubic structure, or if the deformations associated with the structure change were small enough so that the wave propagation characteristics of the crystal were not greatly affected. There is, therefore, some justification in analyzing and presenting the ultrasonic data for the noncubic phase as if it were pseudocubic, although it should be kept in mind that this analysis is not rigorously valid.

At the -151 $^{\circ}\text{C}$ transition there is a step decrease in the electrical conductivity of two orders of magnitude which is reversible upon reheating.¹ Also, new lines appear in the powder x-ray diffraction pattern for the low-temperature phase.⁶ These observations indicate a substantial change in crystal structure at this transition. An attempt to make ultrasonic measurements through this transition was unsuccessful.

IV. RESULTS

Figure 1 shows the results for the shear wave which determines the elastic constant C' which is $\frac{1}{2}(C_{11} - C_{12})$ in terms of the elastic constants referred to the cubic coordinate system. On the left abscissa is plotted the fractional change in the square of the natural wave velocity, W . This is the same as the fractional change in C' , except that the correction for thermal expansion has not been made. The effect of this correction would be to make the slope of this curve more negative by a few percent, but the data to make this correction are not available. The two vertical lines indicate the temperatures of the two phase transitions determined from the centers of two spikes in the specific-heat-vs-temperature data to be -64.3 and -151.4 $^{\circ}\text{C}$.⁷ The data points for the elastic modulus

curve around the -65 $^{\circ}\text{C}$ transition are from several runs while both increasing and decreasing the temperature, and illustrate that the elastic behavior through this transition is reversible with less than 0.2 $^{\circ}\text{C}$ hysteresis if any.

On the right abscissa is the ultrasonic attenuation in $\text{Np}/\mu\text{sec}$. The attenuation is seen to be very flat through the transition region for this wave mode, then it increases sharply well above the -151 $^{\circ}\text{C}$ transition. When the attenuation reaches a value of about 0.5 $\text{Np}/\mu\text{sec}$, each successive echo in the pulse-echo pattern is down by about 17 dB and the wave velocity measurement can no longer be made. When the attenuation reached that value, this run was terminated.

The other shear mode measured gives the elastic constant C_{44} directly. In contrast to the C' shear, the C_{44} shear exhibits a large ultrasonic attenuation peak at -65 $^{\circ}\text{C}$ as is shown in Fig. 2. The peak in attenuation is asymmetric with respect to the transition temperature, the slope of the low-temperature side being much steeper. Again, this behavior was apparently completely reversible with no hysteresis. It is also seen that the elastic modulus C_{44} of the cubic phase anticipates the phase change 40 – 50 $^{\circ}\text{C}$ above the transition temperature, its value falling rapidly as the temperature is decreased. By extrapolating the elastic constants of the two phases to the transition temperature it is seen that there is a 4 – 5% difference, whereas the C' constant changed by less than 1% .

The results for the longitudinal wave mode are shown in Fig. 3. This mode determined the elastic constant C_L , which is $\frac{1}{2}(C_{11} + C_{12} + 2C_{44})$ in terms of elastic constants referred to the cubic coordinate system. For this mode there is again a strong attenuation system. For this mode there is again a strong attenuation peak at the -65 $^{\circ}\text{C}$ transition. The asymmetry of this peak can be seen more readily since it was possible to make measurements over the top of the peak. The