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By

Akira FUKAI and Lawrence M. SLIFKIN*

Abstract

Preliminary measurement of YOUNG's modulus in AgCl at high temperature was carried out by means of the composite oscillator method. Allowed the experimental error due to mismatching in resonance frequency between specimen and quartz resonator, it seems that non-linearity of decrease in YOUNG's modulus with increasing temperature was observed. This contrasts with linear temperature dependence of YOUNG's modulus in alkali halides.

Introduction

It has been well established that, in silver halides, the lattice defect at high temperatures is predominantly of Frenkel type, that is, pairs of lattice defects consisting of interstitial Ag and positive ion vacancies associated with it, although small fraction of defects must be attributed to Schottky type. NICKLOW and YOUNG¹⁾ have recently measured thermal expansion of silver chloride by an x -ray diffraction method and obtained the same results as the dilatometrical data by STRELKOW²⁾, strongly suggesting the predominance of Frenkel defect at high temperatures. A more accurate measurement has been completed by FOUCHAUX and SIMMONS³⁾. For the purpose of quantitative analysis of their data, NICKLOW and YOUNG had to introduce a temperature dependence of the Grüneisen constant. This requirement, however, has already been recognized in the lattice theory of alkali halides in the calculation of properties such as the thermal expansion constant, temperature dependence of compressibility, specific heat, elastic constants, etc.^{4,5)} It is of interest, then, to ask about temperature dependence of elastic constant of silver halides. The work on AgBr⁶⁾ and STEPANOV's work⁷⁾ on AgCl have been reported so far. It is surprising that E_{100} of AgBr decreases near the melting point down to 15% of room temperature value with quite monotonic and negative slope with increasing temperature. Here E_{100} is the YOUNG's modulus along crystallographic direction [100]. On the other hand, the behavior of YOUNG's modulus of AgCl reported by STEPANOV seems erratic.

The present work includes a measurement of YOUNG's modulus (fractional change, not absolute value) as a function of temperature to get more knowledge on the temperature dependence of YOUNG's modulus of AgCl at high temperatures, using the same

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experimental set-up that used for the internal friction work⁸⁾.

Experimental Procedures

Measurements of YOUNG's modulus in the present work were carried out by means of the essentially same apparatus that described in the preceding paper⁹⁾ except some additional components enabling high temperature works. Theoretical background will be briefly presented here with the same notations as used in the preceding paper.

Since YOUNG's modulus of the specimen E_s is related to the resonant frequency of the specimen f_s as

$$E_s = \rho_s (2l_s f_s)^2, \quad (1)$$

we can obtain E_s by knowing f_s . In order to obtain f_s , in turn, we have to know the resonant frequency for the total system f_t and that for background f_q . The relation between these frequencies is given by

$$(m_q + m_s)f_t = m_q f_q + m_s f_s. \quad (2)$$

Assumptions which the derivation of (1) and (2) are based on are: (1) length l_s , the sample length, is more than three times as large as the breadth of the specimen, and (2) f_s must be matched to within 5% of f_q . If one is interested only in the change in YOUNG's modulus (with, say, time) ΔE at constant temperature, then we have simply

$$\Delta E/E_s = 2\Delta f/f_s. \quad (3)$$

On the other hand, if our interest is to obtain the temperature dependence relative to the room temperature value, $E_s/E_{s,R.T.}$, then, by using equation (1),

$$E_s/E_{s,R.T.} = \frac{(f_s/f_{s,R.T.})^2}{1 + \alpha \Delta T}, \quad (4)$$

where $E_{s,R.T.}$ and $f_{s,R.T.}$ are YOUNG's modulus and the resonant frequency at room temperature, respectively, α the coefficient of linear thermal expansion, and ΔT the temperature difference between the measurement temperature and room temperature.

In order to prevent the driver-gauge component from being heated by the furnace surrounding the specimen, a fused transparent quartz rod was used in between specimen and gauge crystal. The fused quartz rods, 3/16" diameter, were matched to the resonant frequency of the driver-gauge crystals to within 0.5%. The final lengths were approximately 16.5 cm, which was expected to correspond to 3/2 times fundamental wave length. The fused quartz rod was mounted at the top end of gauge crystal by beeswax at the center; a small amount of Sauereisen No. 31 cement was additionally applied near the edges to obtain solid joint at higher temperature. Fortunately, even though the joint thus obtained was quite rigid during the first several runs, it ultimately became fragile enough to remove the fused quartz rod quite easily upon complete dry-

ing during the measurements. The joint between the specimen and fused quartz was cemented only by Sauereisen cement, with a room temperature curing for half a day. The furnace was made by winding Nichrome wire, size No. 24, with specific electrical resistance of 1.66 ohm/ft, around a pyrex tube, 1(13/16)" diameter, 1/8" thick, 3(1/2)" long. This furnace was installed such that its center corresponds to that of the mounted specimen when the high temperature set-up is assembled. Vacuum was maintained below 1 micron during the measurements. A chromel-alumel thermocouple was placed inside the furnace as close as possible to the specimen, the distance being 2 to 3 mm. A subsidiary experiment was done to check the temperature difference between specimen and the thermocouple head, in which two thermocouples were used, one of them imbedded at the center of the specimen. A temperature difference of more than 2° was not detected unless the temperature changed at a rate exceeding 25°/hr. With a sufficiently good vacuum, lower than a micron of mercury, inside the enclosure of the composite oscillator, the furnace gave 500°C at the location of thermocouple head. The specimens used in this work were the same that employed in the preceding experiments.

Experimental Data and Discussion

The resonant frequency of the total system has been plotted against specimen temperature, as shown in Figure 1. Since frequency mismatching between specimen and background frequency was observed to be within 5% below 250°C, we can use equation (2) to calculate f_s from the data. At the temperatures above 250°C, the calculation of f_s become complicated. If the same formula is simply used in the whole temperature range, the curve shown in the figure was obtained. The data obtained by using another specimen cut from the same original ingot and parallel to that used in the first run are also shown. The temperature dependence seems to be almost the same in both cases.

We can obtain the relative value of YOUNG's modulus as a function of temperature, $E_s/E_{s,R.T.}$, by using the data in Figure 1 with the help of equation (4). In view of the fact that f_s calculated by equation (2) may involve error due to frequency mismatching, we disregard the small term $(1 + \alpha \Delta T)$ in the denominator in equation (4) which is considered not to change more than 2% for $\Delta T = 430^\circ$. The results thus obtained are shown in Figure 2 where the normalized YOUNG's modulus is plotted against specimen temperature. Due to the hysteresis between data taken with increasing temperatures and decreasing temperatures, there is some ambiguity in the choice between these two. However, since the data of IF-2-6 measured up to 371°C shows no significant hysteresis and since the temperature variation of these data seems close to those of IF-2-5 for increasing temperature, then the upper curve of IF-2-5 is more likely correct. The temperature dependence of elastic constants and stiffness constants of AgCl has been studied by STEPANOV and E'IDUS⁷. There has also been reported the temperature dependence of YOUNG's modulus of AgBr by TANNHAUSER, BRUNER, and LAWSON⁶. For the purpose of comparison, $E_s/E_{s,R.T.}$ were calculated along the same crystallographic orientation as IF-2-5 by using reported elastic constants and

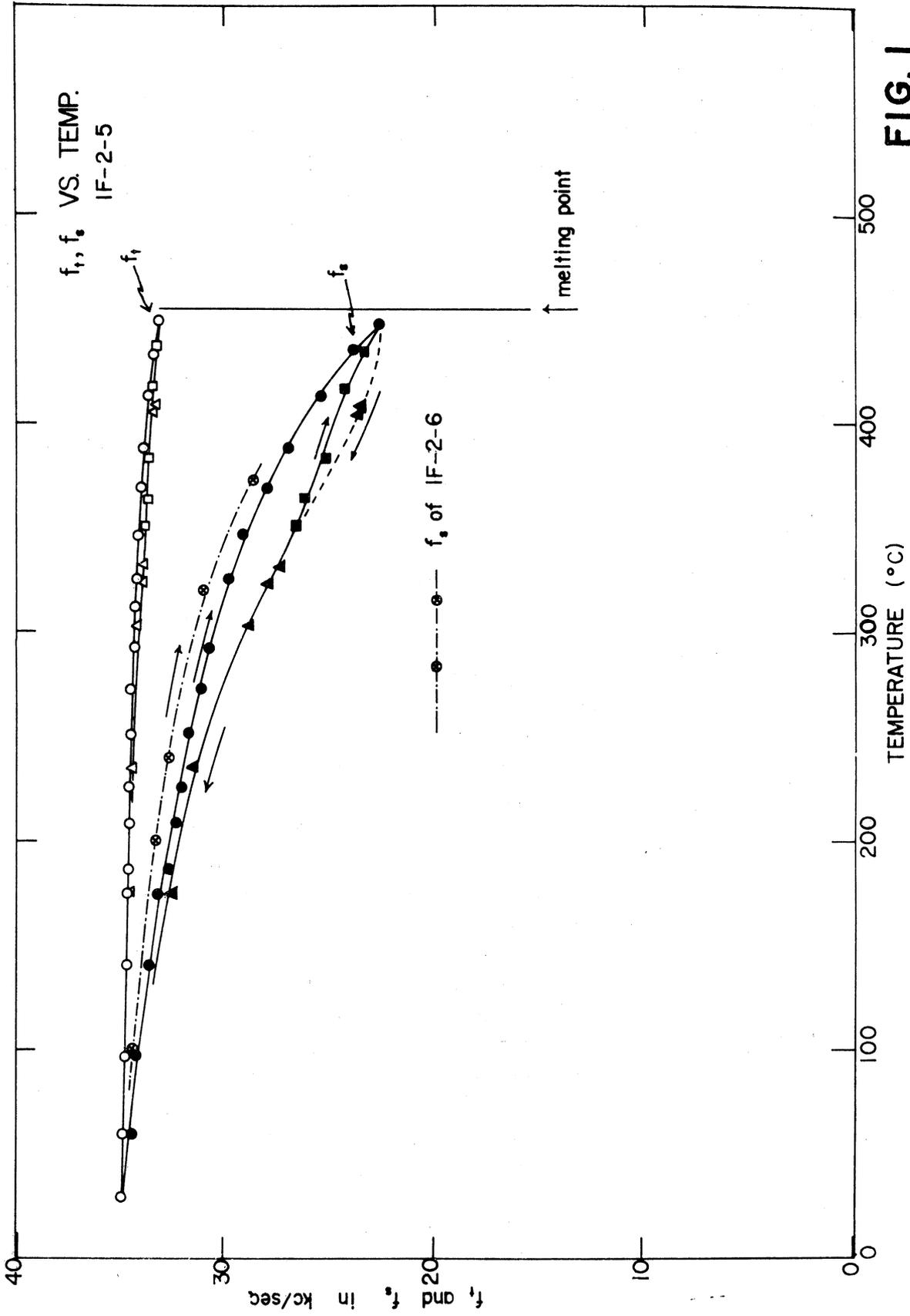


FIG. 1

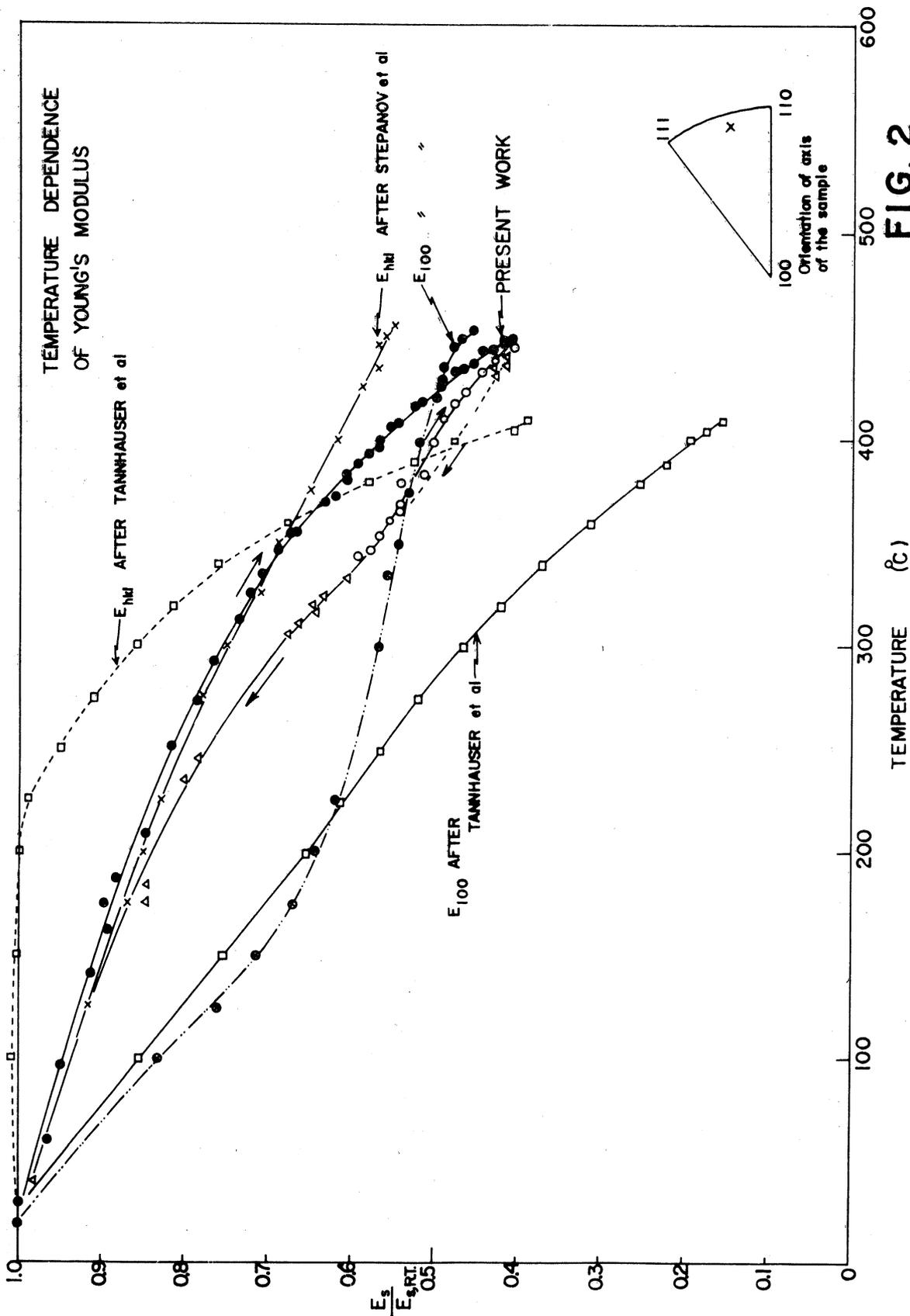


FIG. 2

stiffness constants (6, 7). The results are shown in the figure. E_{hkl} means the YOUNG's modulus in the same crystallographic direction as IF-2-5. E_{hkl} by STEPANOV and E'IDUS agrees quite well with the present work up to 330°C. The temperature dependence of E_{100} by STEPANOV and E'IDUS seems abnormal at temperatures beyond 200°C. E_{hkl} of AgBr is seen to change quite rapidly in the temperature range beyond 200°C. $E_s/E_{s,R.T.}$ in this orientation is the same at the melting points for both AgCl and AgBr. The temperature change of E_{100} is quite marked. In all of these cases, it has been clearly shown that the temperature dependence of YOUNG's modulus is not linear. This is in contrast to alkali halides and metals where the linear variation is almost universal.

It seems premature to speculate the mechanism involved in the data just given above. However, it would be possible to explain the abnormal non-linearity of YOUNG's modulus along the lines of the theory of MITSKEVICH^{4,5)} who treated the thermal and elastic properties in ionic crystals in a modified Grüneisen theory, or as NICKLOW and YOUNG¹⁾ who tried to explain the abnormal lattice expansion in terms of the Grüneisen theory in which Grüneisen constant is not considered constant but temperature dependent. In any event, these large decreases in YOUNG's modulus strikingly indicate anharmonic effect in the silver halides.

Summary

The temperature dependence of YOUNG's modulus has been observed to be quite non-linear, well outside of the error due to frequency mismatching. It is proposed that this non-linearity may be explained in terms of anharmonicity.

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