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Comment on the Elastic Properties of β Brass*

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The Pippard equation relating C_p (the constant-pressure heat capacity) to α (the volume coefficient of thermal expansion) near a λ point is shown to be valid for β brass. As a result of this, one can predict that the static adiabatic compressibility should have a very small peak at T_λ (and the low-frequency elastic constant c_{11}, a small dip). It is suggested that the failure to observe such a dip in c_{11} for 10-Mc/sec ultrasonic waves is due to the long relaxation time associated with ordering in β brass.

THE variation of the elastic moduli of β brass with temperature has been the subject of several experimental studies. These have yielded quite diverse results for the behavior near the order-disorder transition at $T_\lambda \simeq 735°\text{K}$. Work by Rinehart and especially by Artman on the Young's moduli of single crystals indicated that there were anomalous variations near T_λ.[1] Recently, McManus[2] has made ultrasonic measurements at 10 Mc/sec of c_{11}, c_{44}, and $C'=(c_{11}-c_{12})/2$ for a single crystal of CuZn. These new results disagree with the earlier data. McManus reported that both shear constants decrease slightly as the temperature is increased toward T_λ but that c_{11} varies in a smooth, almost-linear fashion throughout the entire transition region.

One would expect that the elastic properties of β brass near its lambda point should strongly resemble those of other solids which undergo cooperative order-disorder transitions. The elastic data necessary for such a comparison are available for ammonium chloride[3] ($T_\lambda = 243°\text{K}$) and for quartz[4,5] ($T_\lambda = 847°\text{K}$). The variation in shear constants is similar in all three of these solids, but the variation in the compressional constants is not. In contrast to β brass, the longitudinal ultrasonic velocities in both NH_4Cl and quartz have a sharp minimum at the lambda point.[6] The following questions arise: (a) should one expect such a dip in c_{11} for β brass, and (b) if so, why is it not observed?

The Pippard equations will be used below to show that a dip is to be expected in c_{11} but that it will be quite small for β brass. In addition, it is proposed that ultrasonic measurements at 10 Mc/sec in β brass yield "frozen" or instantaneous values (infinite frequency limit) rather than static equilibrium values (zero frequency limit).

The Pippard equations,[7] which have been shown to be valid both for ammonium chloride[3] and for quartz,[5] interrelate various equilibrium (static) thermodynamic observables near a lambda point. They are usually written as

$$C_p/T = \xi V\alpha + K_1 \tag{1}$$

and

$$\beta^T = \xi^{-1}\alpha + K_2 , \tag{2}$$

where C_p is the constant-pressure heat capacity, α is the volume coefficient of thermal expansion, β^T is the isothermal compressibility, K_1 and K_2 are constants, and $\xi \equiv (dp/dT)_\lambda$ is the slope of the lambda line. For our purposes it is more convenient to use an expression for β^S, the adiabatic compressibility, instead of Eq. (2). It can easily be shown that

$$\beta^S = K_3 - (K_1/\xi)^2 (T/VC_p) , \tag{3}$$

where K_3 is another constant. The compressibility β^S is related to the adiabatic elastic constants by

$$\beta^S = [c_{11} - (4C'/3)]^{-1} . \tag{4}$$

A plot of Eq. (1) will allow us to determine both ξ and K_1, and thus to calculate the variation expected in β^S near T_λ. Such a plot is shown in Fig. 1. The heat-capacity values were taken from Moser,[8] and the thermal-expansion values were obtained from a smooth curve through the combined data of Steinwehr and

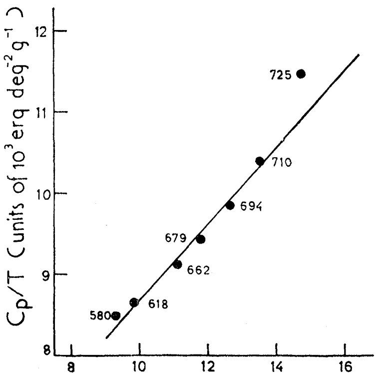

FIG. 1. Pippard plot of C_p/T versus $V\alpha$ for β brass. The temperature (in °K) is given next to each data point. The slope $\xi = 474$ bar deg^{-1} and the intercept $K_1 = 3.92 \times 10^3$ erg deg^{-2} g^{-1}.

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Schulze[9] and Owen and Pickup.[10] These two sets of expansion data are in quite good agreement, considering the experimental difficulties involved. Figure 1 shows that the Pippard equation (1) is valid for β brass, and it is interesting to compare this graph with the analogous plots for NH_4Cl and quartz. For β brass, ξ is large (4.7×10^8 dyn cm^{-2} deg^{-1}) and K_1 is small (3.9×10^3 erg deg^{-2} g^{-1}) compared with either ammonium chloride ($\xi=1.17\times10^8$, $K_1=51\times10^3$) or quartz ($\xi\simeq0.3\times10^8$, $K_1=14.5\times10^3$). Thus $(K_1/\xi)^2$ is 0.7×10^{-10} cm^6 deg^{-2} g^{-2} for β brass, *very small* compared with 1900×10^{-10} for ammonium chloride or 2340×10^{-10} for quartz.

With the above value of $(K_1/\xi)^2$ and Moser's C_p data[8] one can calculate that the right-hand term in Eq. (3) varies from 0.66×10^{-13} cm^2 dyn^{-1} (7% of β^S) at 575°K to 0.48×10^{-13} cm^2 dyn^{-1} (5% of β^S) at 725°K. On this basis, the *peak* in β^S at T_λ should be very small (about 2% above the "normal" value). Even if C_p actually becomes infinite at T_λ, the peak would only amount to about a 6% change in β^S.

Such a predicted peak in β^S would arise from a dip in c_{11} at T_λ. It has been shown elsewhere[11] that a generalized set of Pippard equations in terms of stress-strain variables leads to the prediction that for a cubic crystal C' should not show anomalous behavior due to coupling between mechanical and thermal variables. In any case, the observed variation in C' is small in magnitude and in the wrong direction to cause a peak in β^S. Thus, it is expected that the static c_{11} values for β brass will show a sharp dip at T_λ. But in contrast to ammonium chloride and quartz, this dip will be very small. Some qualitative static measurements[12] of the mechanical properties of β brass seem to indicate a small anomaly near T_λ, but careful work would be needed to definitely establish this effect.

It is suggested that the reason why a dip in c_{11} was not observed by McManus is due primarily to the frequency used in his measurements. For a relaxation theory of irreversible cooperative phenomena,[13] the value of c_{11} will be frequency dependent. *If* $\omega^2\tau^2\gg1$ (where τ is the relaxation time for the ordering process), then the observed c_{11} will represent $c_{11}(\infty)$, the instantaneous value which one expects to vary quite smoothly through the transition region, rather than $c_{11}(0)$, the static value which one expects to show a dip at T_λ. Since changes in ordering in β brass require some kind of atomic diffusion it is very reasonable to expect that τ is rather long.

Indeed, a large τ value would also help to explain the lack of an attenuation peak at T_λ for the 10-Mc/sec data. McManus mentions high attenuation *above* T_λ for all the waves studied, but this is perhaps connected with the fact that the quartz transducer is approaching its α-β transition. Ammonium chloride and quartz show high attenuation for compressional waves both above and *below* T_λ (as does liquid helium also). For the attenuation, one has, according to a relaxation model,

$$2\alpha U=\frac{c_{11}(\infty)-c_{11}(0)}{c_{11}(\omega)}\cdot\frac{\omega^2\tau}{1+\omega^2\tau^2}, \qquad (5)$$

where α is the acoustic attenuation and U is the ultrasonic velocity. If $\omega^2\tau^2\gg1$, then $(\omega^2\tau/1+\omega^2\tau^2)$ becomes simply τ^{-1}. Since it has been predicted that $[c_{11}(\infty)-c_{11}(0)]/c_{11}$ is small and it is assumed that τ is large, one can understand why α is too small to observe at high frequencies. At very low frequencies (~1 cps), a rapid rise in the internal friction of β brass has been observed[14] as the temperature approaches T_λ. This would agree well with the assumption of a long relaxation time.

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