Reply to ‘‘Comment on ‘Light scattering study of the phase transition in sym-triazine’ ’’

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of softening of an acoustic mode associated with an elastice transition is strongly dependent on the direction of the wave vector. This effect could explain the above discrepancies in one or both of two ways. First, the scattering plane is stated[1] to be "almost in the crystal *ab* plane," but if the angle between these two planes is ϕ, the apparent value of c_{44} will be increased by $c_{33}\sin^2\phi$ for small ϕ. Assuming c_{33} to be of the same order of magnitude as c_{11} and estimating the latter quantity from the measured frequency of the longitudinal mode, it is easily shown that the Brillouin and neutron data could be reconciled if ϕ were about 5°. The unique axis of the crystal was indeed tilted by about 5° from the "long crystal axis in the sample cell"[1] and if this misalignment is also relative to the scattering plane it is almost certainly the cause of the discrepancy. Another possibility is that the approximation $c_{14}=0$ may not be correct, particularly in comparison with the small value of c_{44} near the transition temperature. In this case the soft mode velocities would depend on the orientation of the scattering vector in the *ab* plane and the full softening would be observed for particular orientations only. The observed independence of the velocity on a rotation of 90° about *c* would then have to be accounted for by the scattering vector coincidentally lying at ±45° to a symmetry direction in the two cases for which measurements were made, but this explanation has the merit that the observed softening of the higher frequency acoustic mode could then result from its velocity being partly dependent on c_{44} and the need to postulate an independent softening of c_{66} would therefore be avoided.

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Reply to "Comment on 'Light scattering study of the phase transition in *sym*-triazine' "

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Rae's comment (preceding paper)[1] on our recent paper concerning the phase transition in *sym*-triazine[2] contains four main points. These are as follows: (1) the neutron data show a factor of 3.7 greater softening than do the Brillouin data; (2) the proper value of the mean field parameter T_1 is 193 K not 180 K ($T_0=-759$); (3) these two differences can be attributed to inadequacies in the Brillouin data and approximations in their interpretation; and (4) there is only one soft mode in *sym*-triazine characterized by c_{44}. Below we address each of these issues separately.

(1) Neutron vs Brillouin softening. Neutron data for the phonon groups at $q=0.1a_h^*$ ($1.0339\times10^{+7}$ cm^{-1}) polarized along c_h and measured at $\mathbf{Q}=(-0.9, 0, 2)$[3] do evidence a larger softening than the Brillouin data obtained at $q=1.9436\times10^{+4}$ cm^{-1}. The extrapolation from one set of results to another, especially for the absolute magnitude of the softening, is difficult at best in the presence of a phase transition. It seems that the only important point is the relative change in ω with temperature for which both sets of results are in complete agreement.

(2) Value of the mean field parameter T_1. In fitting the experimental results to a mean field theory, many of the Hamiltonian parameters are set to zero[4]; this must be remembered in looking at any one parameter. To extract a quantitative fit or to decide whether the various approximations are appropriate, more data are always useful. However, the accuracy of all previous measurements (including x-ray, Brillouin, and neutron) probably are not sufficient to determine even a few parameters to better than 5%. To make this point clear to the reader we present Fig. 1 with various fits to the x-ray and neutron data. The x-ray data are analyzed as uniquely giving the order parameter e_5 under the assumption that the e_1-e_2 strain is zero. This is clearly only approximate [see point (4) concerning c_{66} (e_1-e_2) softening] and evaluation of the e_1-e_2 strain could alter the value for $T_1\pm5\%$. It should also be noted that fits[6] to the heat capacity data,[7] using the theory of Ref. 4, arrive at parameters $T_1=185$ K and $T_0=-759$ K. We conclude therefore that all data are reasonably fit to a value of T_1 falling between 180 and 190 K.

(3) Brillouin data collection and interpretation. We have made the points[2] that the scattering plane may be displaced by 5° and that the analysis of our Brillouin data rests on the approximation that $c_{14}=0$. Indeed, many other approximations have been made in the form of setting various coupling parameters to zero in our Hamiltonian; of course, the values of the presented parameters depend on these approximations. It is, furthermore, implicit in the presentation that neither c_{44}

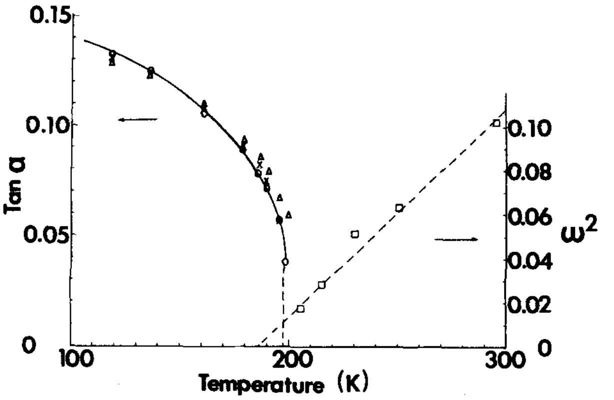

FIG. 1. A plot of the strain data (e_5 with $e_1 - e_2 = 0$) and the neutron scattering phonon groups ω^2 vs temperature. For the strain, tan α (*lh* side), the experimental data (Ref. 5) are given by o's and the full line is the least squares fit for $T_1 = 193$ K and $T_0 = -759$ K. The ×'s are theoretical fits for $T_1 = 180$ K and $T_0 = -759$ K with the experimental point at 198 K omitted from the fit; heat capacity data (Ref. 7) indicated that this point should have large contributions from non mean field sources. The ▵'s are a fit using all experimental points. The □'s are the ω^2 values obtained from neutron scattering data (Ref. 3) uncorrected for dispersion. The dashed line through these points is one of many that can be drawn for the data ($180 < T_1 < 190$ K).

or c_{66} represent the true soft mode for this crystal, and some rather complicated q dependent mixture of the two is needed.

(4) The only soft mode is characterized by c_{44}. This can be demonstrated to be incorrect by solving the dynamical matrix for *sym*-triazine. Following Rae's suggestion ($\phi = \pm 45$, $c_{14} \neq 0$), a perturbation technique yields expressions which give too small a change in c_{66} for appropriate values of the constants and with these assumptions the c_{44} behavior is not correct. Moreover, one predicts that a ±45° orientation of the crystal in the *ab* plane should leave the spectra unchanged. Experimentally it is found that under an *ab* plane 90° crystal rotation, other features in the spectrum change dramatically in intensity while the soft mode remains essentially unchanged. Thus, two *independent* soft modes must exist in *sym*-triazine with different T_1 values (~180 and ~17 K). The presence of this extra soft mode will of course affect the values of the various parameters obtained from x-ray strain measurements; in the analysis of these data only e_5 was assumed to be finite.[5] A similar situation has been observed for benzil.[8]

Rae's comment not withstanding, it appears as though the neutron, Brillouin, heat capacity, and x-ray strain data are in reasonable agreement with the two parameters $180 < T_1 < 190$ K (±5%) and $T_0 = -759$ K for the mode governed mainly by c_{44} (e_5). Another soft mode, mainly governed by c_{66} (e_1-e_2), has the same T_0 and $T_1 \sim 17$ K. These results are in quite good agreement with mean field theory[4] considering the approximations made in data analysis ($c_{14} \simeq 0$, $(e_1$-$e_2) \approx 0$, etc.) and the approximations made in the theoretical analysis (only a few of the potential parameters in $\mathcal{H}$ are not zero).

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Comments on "Scaling theory and enthalpy of mixing for binary fluids"

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In a recent note, ten Brinke and Karasz[1] have discussed the character of the enthalpy of mixing for binary mixtures near a critical solution temperature (UCST for an upper temperature and LCST for a lower one). They have shown that many of the qualitative features indicated by the classical model of fluids[2,3] are retained by the scaling model. The real emphasis should not fall on the model but on the stability criterion demanded by the second law of thermodynamics, from which the same conclusions can be drawn.

The consequences of that criterion, that in a binary mixture $(\partial^2 G/\partial x^2)_{T,p} \geq 0$, can readily be shown with four simple figures and a brief geometrical argument. Figures 1(a) and 1(b) refer to UCST's; Figs. 2(a) and 2(b), to LCST's. Figures 1(a) and 2(a) refer to positive values for dT_c/dp; Figs. 1(b) and 2(b), to negative values for dT_c/dp. In these four figures, lines of constant $(\partial^2 G/\partial x^2)_{T,p}$ are shown for the critical composition, which, for the sake of argument, is assumed a constant. The stability criterion requires that, as one "moves" into the stable one-phase region "away" from the critical line, the value of $(\partial^2 G/\partial x^2)_{T,p}$, which is zero on that line, not decrease but become progressively more positive. In the figures, the values of $(\partial^2 G/\partial x^2)_{T,p}$ are shown becoming more positive (0 → + → ++ → +++, etc.) the farther they are from the critical line. As a consequence, we find that