

## Elastic Constants and Debye Temperature in $\text{LaCl}_3$

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## Elastic Constants and Debye Temperature in $\text{LaCl}_3$

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During the process of interpreting pressure effects in NQR for some rare earth trichlorides,<sup>1</sup> we were led to examine the elastic constants of  $\text{LaCl}_3$  calculated by Stedman and Newman.<sup>2</sup> These constants proved to be inconsistent with low temperature thermal data. Since this inconsistency has far-reaching consequences, not only for our work but also for others concerned with the elastic behavior of  $\text{LaCl}_3$ , we deem it appropriate to examine this fact in a separate note.

Using the three sets of elastic stiffness constants in Stedman and Newman (denoted by them as  $\mathcal{L}$ ,  $\mathcal{N}$ , and  $\mathcal{C}$ ) and the values published by Walcott<sup>3</sup> we obtain for the Debye temperature  $\Theta_{\text{Debye}} \approx 400$ , 300, and 370°K, respectively. The experimental value obtained from low temperature specific heat data<sup>4</sup> is  $149.5 \pm 1.5^\circ\text{K}$ . The disagreement for crystals that depend on between values based on valid calorimetric and elastic data. The factor of 3 needed for agreement can be obtained by changing the 5 independent elastic constants in many different ways. Two extreme methods of change serve to illustrate some specific consequences.

One extreme is to maintain the ratios between elastic constants but scale all constants down by a factor of 16. Then the macroscopic compressibilities increase by a factor of 16, the sound velocities decrease by a factor of 4, and the bulk compressibility changes from the range appropriate for transition oxides to the range appropriate for the cubic alkali halides.

A second extreme is to change a single elastic constant. The most effective realization of this method is to increase  $C_{11}$  until it is slightly less than  $C_{12}$ . The bulk compressibility does not change significantly and the linear compressibilities change by a factor of 3 or less. In each instance the original set of elastic constants results in lower compressibility along the  $c$  axis being smaller than that along the  $a$  axis, and the altered set reverses this result. More strikingly, this method of changing the elastic constants decreases the velocity of one sound mode by a factor of 4 which it demonstrates the expression for the Debye temperature. That is, a soft mode would be present which would

suggest some macroscopic effect such as an incommensurate phase transition or a phase of easy cleavage. Such macroscopic effects are not yet observed, and we believe that an appropriate scaling of the elastic constants is a more probable explanation.

The significance of such changes for the subsequent rate results of Stedman and Newman is very difficult to ascertain. This difficulty is best illustrated by considering their averaged velocity,  $\bar{v}$ , and its given value,  $1.32 (10^3)$  cm/sec. Use of this value produces  $\Theta_{\text{Debye}} \approx 180^\circ\text{K}$  which is in reasonable agreement with that derived from thermal data but is totally inconsistent with the given elastic constants. The crux of the disagreement lies in the manner of calculating  $\bar{v}$ . Stedman and Newman use

$$\langle \bar{v} \rangle = 1 / \left( \sum_i 1/v_i^3 \right)^{1/3} \quad (1)$$

which is appropriate for Raman rates while the Debye temperature calculation requires

$$\langle \bar{v} \rangle = 1 / \left( \sum_i 1/v_i \right) \quad (2)$$

where  $\langle \rangle$  denotes an average over all directions. Both  $\bar{v}$  and the Raman rates are very sensitive to velocity distributions, but their functional forms are quite different and care is essential when attempting to make averages deduced from these phenomena. Thus, although altered elastic constants are essential to agree with the experimental data, the variety of acceptable situations provide no unique result for Eq. (1) and hence for the Raman rates.

The significance for macroscopic elastic behavior is both clear and dramatic. Compressibilities might be about 15 times larger than indicated or else the application of hydrostatic pressure might cause a 3/4 mile change of either sign.

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## Comparison of Accurate Quantum-Mechanical Probabilities with Classical and Transition-State Theory Results for the Collinear Exchange Reaction $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$

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The reaction  $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$  is of fundamental importance in theoretical studies of the dynamics of chemical reactions since it is the simplest example of the simplest type of reaction ( $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$ ). It has been the object of many investigations ranging from classical collision to quantum-mechanical three-dimensional treatments.<sup>1</sup> A model commonly employed is that of the collinear, electronically adiabatic collision along the three-particle line.<sup>2</sup> With this model, we compare the results of accurate classical and quantum-mechanical calculations of the reaction probabilities for the  $\text{H} + \text{H}_2$  reaction on the analytic semiempirical potential surface of FOCUS and Karpus<sup>3</sup>; this surface has a symmetric saddle-point barrier of 0.996 eV (relative to  $\text{H} + \text{H}_2$ ) with internuclear distances of 0.90 Å.

The classical transition probabilities were calculated by Martin Cates average over a large number of trajectories,<sup>4</sup> in which the reacting molecule had zero-point vibrational energy. The quantum probabilities were obtained by numerical integration of the relevant three-coupled equations<sup>5</sup>; the parameters of the integration were fixed so that the probabilities are precise within 1%. Figure 1 shows plots of total reaction probability versus relative translational energy for ground-state  $\text{H}_2$ . The general behavior of the obtained (CM) and quan-

tum-mechanical (QM) curves is similar, although there are notable differences. The most important is that the effective QM threshold is about 0.07 eV lower than the CM threshold and that the QM reaction probability remains consistently larger than the CM result up to about 0.3 eV. This difference, if carried over to a three-dimensional treatment, would, of course, lead to significant tunneling corrections in the thermal rate constant. At higher energies, both probabilities fall off, but the CM curve shows no indication of the steep QM dip just above threshold for vibrational excitation.<sup>6</sup>

Figure 2 shows a comparison of the exact QM reaction probability with a weighted average QM probability calculated from the rate constant of absolute rate theory<sup>7</sup> assuming the transmission coefficient to be unity and neglecting tunneling; this latter curve (ART) is a step function with a value of unity above threshold, in the energy sense considered. To include tunneling the ART probability has to be corrected for the transmission coefficient of a single particle hopping over a one-dimensional barrier representing the effective potential surface for the reaction. The results for the tunneling correction depend on the (a) choice of

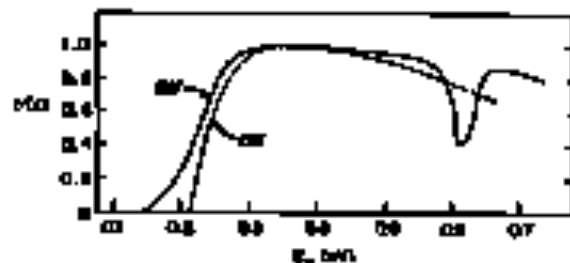


FIG. 1. Reaction probability versus relative translational energy for ground-state  $\text{H}_2$ .

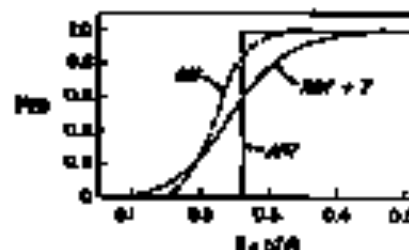


FIG. 2. Comparison of weighted average quantum-mechanical reaction probability from transition-state theory with the exact quantum-mechanical probability. ART—no tunneling correction; ART-T—Stern tunneling correction (see text).