

## Multiphonon infrared absorption in the transparent regime of alkaline-earth fluorides

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We present an experimental investigation of the frequency and temperature dependence of the multiphonon infrared absorption coefficient in the alkaline-earth fluorides  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$ . Over the range investigated, a nearly structureless, exponential-like behavior is found for the frequency dependence of the absorption, and a Bose-Einstein-like multiphonon behavior for the temperature dependence. The data are analyzed employing a simplified model of multiphonon absorption; the overall agreement with experiment is quite good, although various discrepancies are present. We conclude that alkaline-earth fluorides do indeed display intrinsic multiphonon absorption over an extended frequency and temperature range, and we determine the parameters governing this behavior.

### I. INTRODUCTION

The alkaline-earth fluorides are promising candidate materials for infrared applications requiring optical components of high transparency.<sup>1</sup> The limiting absorption in the transparent-frequency ( $\omega$ ) regime above the reststrahl in ionic solids stems from intrinsic multiphonon processes. Thus, detailed knowledge of the multiphonon infrared absorption coefficient  $\alpha(\omega, T)$ , where  $T$  is temperature, is of paramount importance. The latter has been investigated extensively in a wide variety of materials,<sup>2-5</sup> including the alkaline-earth fluorides,<sup>6,7</sup> and theoretical analyses have been pursued as well.<sup>8-14</sup> The present work provides the first detailed experimental investigations of  $\alpha(\omega, T)$  for  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  over extended frequency and temperature ranges. The results are analyzed in terms of a simplified model of multiphonon absorption. A preliminary account of aspects of this work was presented previously.<sup>15</sup>

Recent investigations of  $\alpha(\omega, T)$ <sup>3,4</sup> have demonstrated that in ionic solids  $\alpha$  decreases nearly exponentially with increasing frequency over the range typically accessible to measurement (one to four phonons). Moreover, at room temperature and above very little structure is manifested by  $\alpha(\omega)$  within or beyond the three-phonon regime. The observed  $T$  dependence in the many-phonon regime<sup>16</sup> is substantially less than that predicted for intrinsic multiphonon processes, a result which has been interpreted in terms of the  $T$  dependence of the phonon spectrum.<sup>17-21</sup> We will here find analogous behavior for the  $\omega$  and  $T$  dependence of  $\alpha$  in the transparent regime of alkaline-earth fluorides. However, the  $T$  dependence of the phonon spectrum will play a lesser role, because the frequencies  $\omega/\omega_{\text{TO}}$  considered here are much smaller than those in the halide experi-

ments; moreover, thermal-expansion effects are smaller for fluorites than for alkali halides.

### II. EXPERIMENTAL PROCEDURE AND RESULTS

Single-crystal fluorite samples, 1.90 cm in diameter, with the following polished thicknesses ( $\text{CaF}_2$ , 0.645 and 1.285 cm;  $\text{SrF}_2$ , 0.334 and 1.640 cm; and  $\text{BaF}_2$ , 0.291 and 1.416 cm) cut from long (5–10-cm) rods of high-purity Optovac material were used for the investigations at elevated temperatures. The room-temperature transmissions of these samples, as well as those of the original rods with polished ends, were determined with a Beckman IR-7 spectrometer. The long-sample measurements were used to extend room-temperature data to the range of lower absorption coefficients (higher frequencies) and to detect the possible presence of weak impurity bands. The room-temperature spectrophotometric measurements did not reveal any impurity bands in the frequency region investigated.

To obtain the transmissions at elevated temperatures the exit beam from a Perkin-Elmer Model 98 spectrometer equipped with a NaCl prism was focused on a sample positioned at the center of a wire-wound tube furnace and the transmitted beam was collected and imaged on a thermocouple detector. A thermocouple was employed since it was found to be less affected by fluctuations in background thermal radiation than more sensitive photoconductive detectors. Sample temperatures were measured with a Cu-constantan thermocouple placed at the edge of the sample and were monitored by a Doric digital thermocouple meter. At temperatures above 670°K an extended Cu-constantan calibration was used.<sup>22</sup> The furnace was allowed to stabilize at each temperature before measurement. The temperature variation

during measurement was less than  $\pm 5^\circ\text{C}$  at the highest temperature ( $800^\circ\text{K}$ ). The initial temperature gradient between the edge and the center of the sample was found to be approximately  $15^\circ\text{K}$  at the highest temperature but became almost negligible after a stabilization period of about 1 h. The entire furnace was baffled with firebrick to keep direct thermal radiation from reaching the detection thermocouple.

Optical transmission measurements were made by an in-out technique with the  $I_0$  level measured throughout the spectral range at each temperature in order to minimize the effects of small intensity changes arising from the shift of sample and furnace emission peaks with temperature. The measurements were carried out at frequencies between  $700$  and  $1600\text{ cm}^{-1}$  over a temperature range of  $295$ – $800^\circ\text{K}$ . Absorption values were determined from the transmission measurements utilizing a computer program which relates absorption, transmission, reflectivity, and sample thickness, taking multiple internal reflections into account.<sup>23</sup> The reflectivity used for these computations was determined in each case from the maximum transmission in a frequency range where absorption is negligible. Refractive-index variations with frequency and temperature in the ranges of interest were estimated to be small and were not taken into account. With the long optical path involved some error in determining the maximum transmission can be introduced by even small variations in position of the sample in the furnace. A comparison of room-temperature data obtained for samples measured both in the furnace and with the Beckman IR-7 spectrophotometer indicated differences of up to 5% in absorption values in some frequency regions.

To provide an additional check of absorption variation with temperature at a single frequency, transmissions of the  $0.334\text{-cm}$   $\text{SrF}_2$  and  $0.291\text{-cm}$

$\text{BaF}_2$  samples were also determined at the  $10.6\text{-}\mu\text{m}$   $\text{CO}_2$  laser frequency by directing the beam through the sample in the furnace as it was heated from room temperature to  $800^\circ\text{K}$ . Incident and transmitted laser power were measured by a Coherent Radiation 201 power meter, and temperature at the edge of the sample was recorded continuously during the heating cycle. Calorimetric measurements made at the laser frequency ( $943\text{ cm}^{-1}$ ) with 2–3-W power levels indicated a rapid rise in temperature due to laser heating, particularly with the larger absorption coefficients found for  $\text{SrF}_2$  and  $\text{BaF}_2$  at the higher temperatures. This implies that, with the present laser beam to sample diameter ratio of 1:3 and the power levels employed, the center of the sample may be locally heated to a higher temperature than that indicated by a thermocouple placed at the edge. This effect, which will be more pronounced if insufficient time is allowed for the sample temperature to stabilize, may introduce an uncertainty in the measured temperature and lead to a possible discrepancy between laser and spectrometer absorption values. Thus the laser measurements are believed useful as qualitative rather than quantitative checks on the spectrometer data.

The results of spectrometer measurements of  $\alpha(\omega, T)$  for  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  samples are indicated in Fig. 1. These results display the typical exponential-like decrease in  $\alpha$  vs  $\omega$ , which we analyze in some detail in Sec. III. In general, these curves appear very similar to those presented previously for alkali halides by Barker.<sup>24</sup>

Laser transmission data for  $\text{BaF}_2$  and  $\text{SrF}_2$  are indicated in Fig. 2 along with our spectrometer data, and the laser data of Chen *et al.*<sup>7</sup> for comparison. Although some deviations are observed at the higher temperatures, possibly for the reason indicated previously, the various data are nevertheless seen to agree quite well overall.

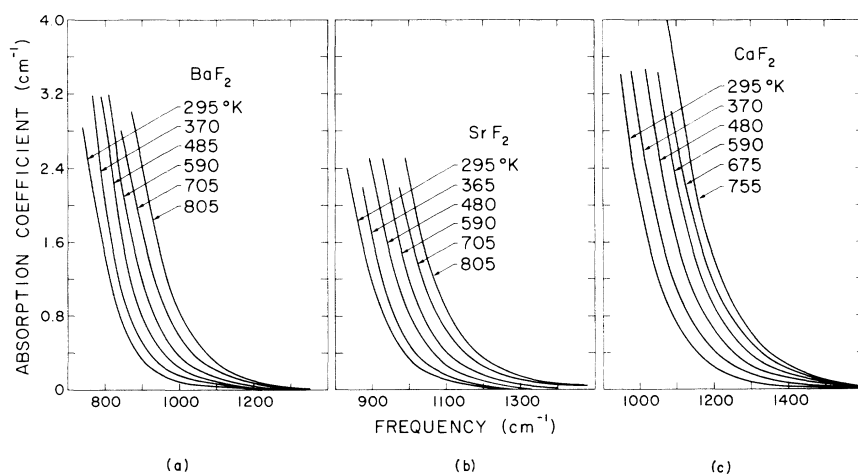


FIG. 1. Measured absorption coefficient versus frequency for alkaline-earth fluorides at various temperatures: (a)  $\text{BaF}_2$ , (b)  $\text{SrF}_2$ , and (c)  $\text{CaF}_2$ .

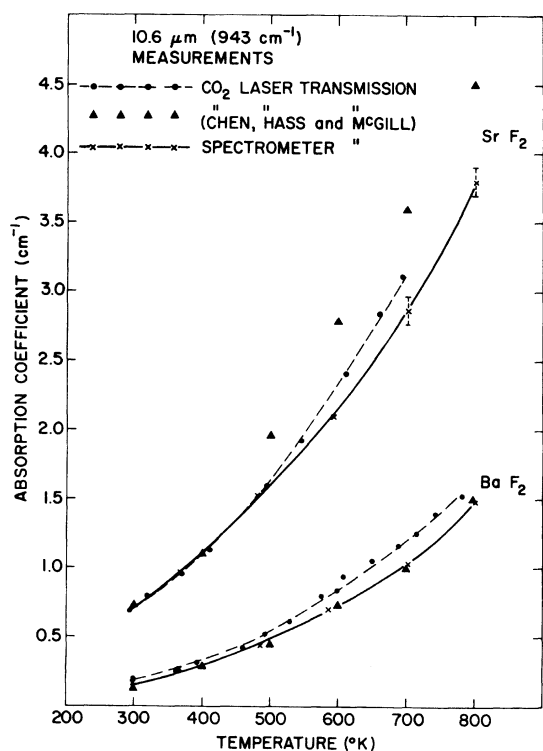


FIG. 2. Comparison of absorption versus temperature of  $\text{BaF}_2$  and  $\text{SrF}_2$  as determined by  $\text{CO}_2$ -laser measurements and by spectrometer transmission measurements at  $10.6 \mu\text{m}$ .

### III. DISCUSSION

As mentioned in Sec. I, ionic solids are characterized by a relatively structureless exponential-like  $\alpha$  vs  $\omega$ . In Fig. 3 we plot the room-temperature absorption of the three crystals on a logarithmic scale versus frequency, along with data of Deutsch.<sup>3</sup> Our data agree reasonably well with the latter, and both are seen to fall nearly on straight lines. In Fig. 4 we plot the absorption on a logarithmic scale vs  $\omega$  for  $\text{BaF}_2$  at various temperatures, from which it can be seen that the exponential-like behavior of  $\alpha(\omega)$  is preserved at elevated  $T$ .

To interpret the room-temperature data, we can utilize the results of calculations for fluorites performed earlier by Namjoshi *et al.*,<sup>6</sup> in which the absorption is related to a sum over  $n$ -phonon densities of state, weighted by coefficients determined from the interionic potential. The details are described in the latter reference; we here merely display the results as the solid lines in Fig. 3. The agreement between theory and experiment is observed to be quite good.

Although one could, in principle, utilize the approach of Namjoshi and Mitra<sup>13</sup> as well as those

of others which properly incorporate detailed crystalline properties<sup>8,9,12</sup> to interpret the high-temperature spectra, such treatments tend to become cumbersome and unwieldy. In general, we require the temperature dependence of all optical phonons, and we must incorporate these into the calculated  $n$ -phonon densities of state. We have therefore chosen to analyze the present results in terms of a more approximate but substantially simpler approach which is based on the properties of an average oscillator for the phonons.<sup>9</sup> We note that this approach has previously provided good agreement with experiment for the alkali halides,<sup>25</sup>

Following Bendow,<sup>9</sup> we express the absorption in terms of a suitable effective phonon frequency  $\omega_0(T)$  with an appropriate average  $T$  dependence, the choice of which will be discussed in more detail below. One has

$$\alpha(\omega, T) = \alpha_0 \frac{[n(\omega_0(T)) + 1]^{\omega/\omega_0(T)}}{n(\omega) + 1} \exp[-A\omega/\omega_0(T)]$$

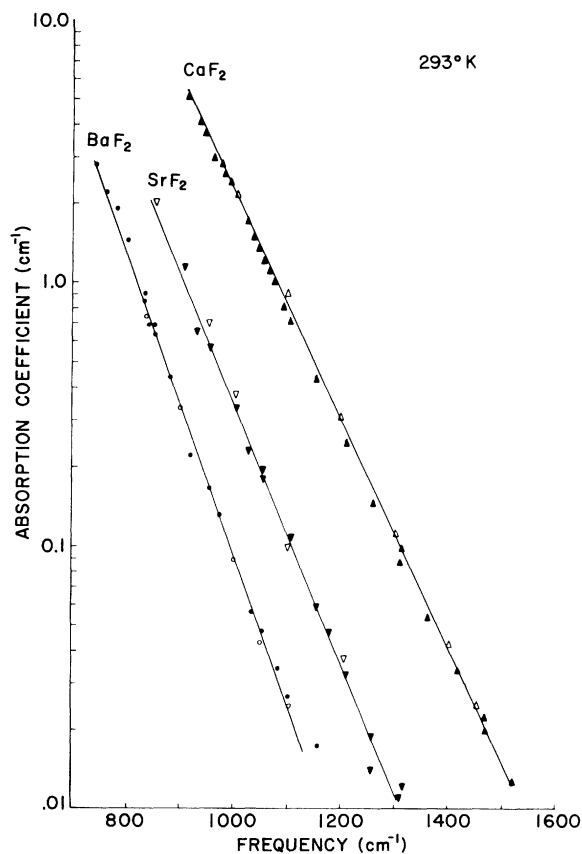


FIG. 3. Room-temperature absorption coefficient versus frequency for alkaline-earth fluorides. Solid symbols, present data; open symbols, data of Deutsch (Ref. 3); solid lines, theoretical calculations from Ref. 6.

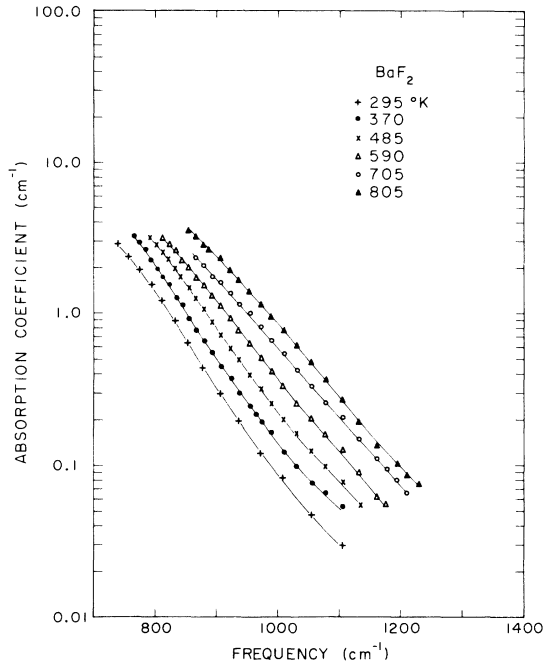


FIG. 4. Measured absorption coefficient versus frequency plotted on a semilog scale to demonstrate the persistence of the exponential-like character of the absorption at elevated temperatures.

$$= \alpha_0 \frac{\exp\left\{-A + \ln[n(\omega_0(T)) + 1]\right\} \omega / \omega_0(T)}{n(\omega) + 1} \quad (1)$$

$$n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1},$$

where  $\alpha_0$  and  $A$  depend weakly on  $\omega_0$  and/or  $T$ . From the above formula, it is clear that  $\alpha$  is enhanced at high  $T$  according to the usual  $T^{j-1}$  law for a  $j(=\omega/\omega_0)$ -phonon process, provided that  $\omega_0$  is independent of temperature. In general,  $\omega_0(T)$  decreases with increasing  $T$ , which tends to suppress the  $T$  dependence of  $\alpha$  arising from the Bose-Einstein factors  $[n(\omega_0) + 1]^{\omega/\omega_0}$ .

To apply Eq. (1) we must specify the effective oscillator frequency  $\omega_0(T)$ . Because the contributions of acoustic phonons are suppressed due to energy conservation, the average frequency  $\bar{\omega}$  defined by the first moment of the density of states should not be an appropriate choice. On the other hand, an average optical phonon frequency, such as the Brout frequency<sup>26</sup>  $\omega_B$ , should be more appropriate. For the present case,

$$\omega_B = \left[\frac{1}{6}(2\omega_{TO}^2 + \omega_{LO}^2 + 3\omega_R^2)\right]^{1/2}, \quad (2)$$

where  $\omega_R$  is the Raman frequency. It turns out that  $\omega_B$  is close to the Debye frequency  $\omega_D$  for most polyatomic crystals and that both are related to the bulk modulus; values for the characteristic frequencies for the fluorites are listed in Table I. Regarding the  $T$  dependence of  $\omega_0$ , we note that

for ionic solids the principal  $T$  dependence arises from thermal-expansion effects, so that one obtains<sup>26</sup>

$$\omega_i(T) \approx \omega_i(0) \exp\left(-3\gamma_i \int_0^T \alpha_T dT\right), \quad (3)$$

where  $\alpha_T$  is the coefficient of linear expansion and  $\gamma_i$  the mode Grüneisen parameter. A more exact theory would account for the effects of anharmonicity on the  $T$  dependence, but fortunately cancellations between the contributions of cubic and quartic anharmonicities tend to suppress anharmonic effects in most cases. Extending Eq. (3) to the average oscillator yields

$$\omega_0(T) = \omega_0(0) \exp\left(-3\gamma_0 \int_0^T \alpha_T dT\right), \quad (4)$$

where  $\gamma_0$  is now a suitably averaged (macroscopic) Grüneisen parameter. The obvious choice of  $\gamma$  corresponding to  $\bar{\omega}$  is the thermal average<sup>27</sup>

$$\bar{\gamma} = \frac{\sum_i C_i \gamma_i}{\sum_i C_i}, \quad (5)$$

where the  $C_i$ 's are Einstein heat capacities and the sum is over all modes of the crystal. If one utilizes  $\omega_D$  for  $\omega_0$ , then<sup>28</sup>

$$\gamma_D = -\frac{d \ln \omega_D}{d \ln V} = -\frac{3\alpha_T V B}{C_v}, \quad (6)$$

where  $B$  is the isothermal bulk modulus and  $C_v$  the specific heat at constant volume.  $\bar{\gamma}$  and  $\gamma_D$  are usually very close in value, as demonstrated for  $\text{CaF}_2$  by Ganesan<sup>29</sup> and for  $\text{SrF}_2$  and  $\text{BaF}_2$  by Vetelino.<sup>30</sup> The  $\gamma$  corresponding to  $\omega_B$  follows

TABLE I. Characteristic phonon frequencies ( $\text{cm}^{-1}$ ) and Grüneisen constants for alkaline-earth fluorides.

	$\text{CaF}_2$	$\text{SrF}_2$	$\text{BaF}_2$
$\omega_{TO}^a$	261	223	188
$\omega_{LO}^a$	482	395	344
$\omega_R^b$	322	283	243
$\omega_B$	337	288	247
$\omega_D$	329 <sup>c</sup>	288–299 <sup>d</sup>	215–240 <sup>d</sup>
$\bar{\omega}$	315	280	255
$\omega_0$	259 <sup>e</sup>	...	237 <sup>f</sup>
$\gamma_B$	1.85	1.86	1.85

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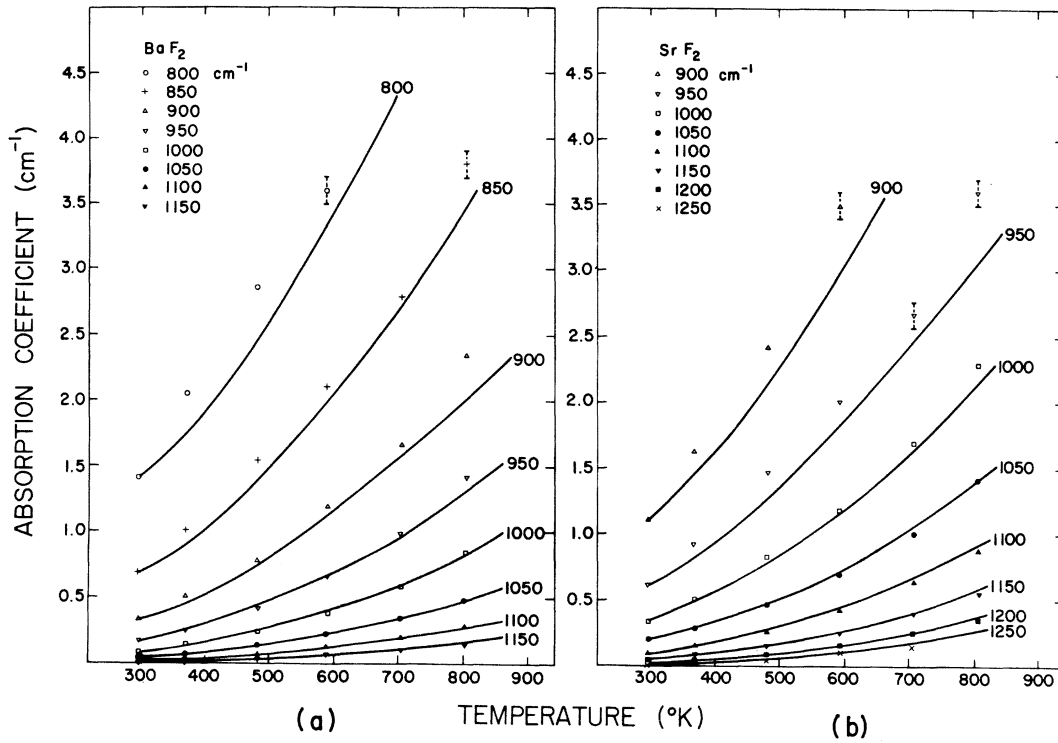


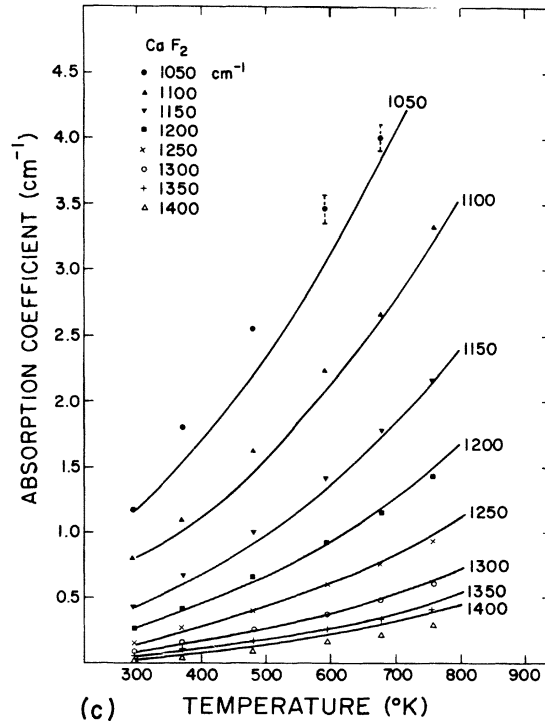
FIG. 5. Absorption coefficient versus temperature for (a)  $\text{BaF}_2$ , (b)  $\text{SrF}_2$ , and (c)  $\text{CaF}_2$ , at various representative frequencies. The solid lines are calculations obtained from Eq. (1) utilizing  $\omega_0$  values given in Table I, while the individual points are experimental data. Values designated with error bars are obtained by extrapolating the logarithm of the measured absorption versus frequency curve at that temperature.

directly as

$$\gamma_B = \frac{1}{6} \left( \gamma_{LO} \frac{\omega_{LO}^2}{\omega_B^2} + 2\gamma_{TO} \frac{\omega_{TO}^2}{\omega_B^2} + 3\gamma_R \frac{\omega_R^2}{\omega_B^2} \right); \quad (7)$$

The value of  $\gamma_B$ , which is listed in Table I, is close to that of the other  $\gamma$ 's as well.

We have performed numerical computations utilizing the values of Table I in Eq. (1) to analyze the experimental data. Since the constants  $\alpha_0$  and  $A$  were determined from the room-temperature spectra (see Fig. 3), in principle no adjustable parameters appear in the computations. We find that the use of  $\bar{\omega}$  for  $\omega_0$  leads to too strong a  $T$  dependence for  $\alpha$ , while use of  $\omega_R$ ,  $\omega_D$ , or  $\omega_B$  gives an improved but not perfect fit. These results imply that acoustic phonons have a relatively minor influence on the multiphonon absorption, and that  $\alpha$  is best characterized by an average optical phonon. The latter conclusions are consistent with the results of other related analyses as well.<sup>4,25</sup> Regarding  $\gamma$ , it was found that for the range of frequencies of interest here  $\alpha(T)$



was relatively insensitive to the particular  $\gamma$  chosen.

To test the wider applicability of Eq. (1) to the present case, calculations of  $\alpha(T)$  were performed for the three fluorides using values of

$\omega_0 \sim \omega_B$ . It was not possible to obtain good agreement over the full range of frequencies in all cases when a single fixed  $\omega_0$  was utilized; rather, to obtain the best fit it would have been necessary to increase  $\omega_0$  with increasing frequency. This suggests that at lower frequencies more acoustic (or, in general, lower-energy phonons) take part in the absorption. However, such a variation of  $\omega_0$  with frequency is not contained in Eq. (1) and does not provide a consistent basis for interpretation of the data utilizing this equation. We therefore chose to search for the single  $\omega_0$  which gave the best fit to the entire set of data for each solid.  $\gamma_B$  of Eq. (7) was utilized for  $\gamma$ , with  $\gamma_{TO}$  taken from Ref. 31,  $\gamma_R$  from Ref. 32, and with  $\gamma_{LO}$  estimated utilizing the method of Ref. 33. The values obtained for  $\omega_0$  are indicated in Table I and are seen to lie quite close ( $\approx 5\%$ ) to  $\omega_B$ . The calculated  $\alpha$ 's for these values are displayed in Fig. 5. The agreement with experiment is excellent for  $\text{BaF}_2$  and quite good for  $\text{SrF}_2$ . The fit is qualitatively, but not quantitatively, adequate for  $\text{CaF}_2$  over the full range of frequencies. While the origin of the discrepancies is not clear,

it must be realized that the higher-frequency (low  $\alpha$ ) data where the largest disparities occur are, in fact, the most susceptible to experimental error. Moreover, Eq. (1) which we have utilized here does not take detailed account of selection rules and/or density of state effects<sup>12,13,26</sup> and may well be inadequate for a quantitative analysis over a wide range of frequencies and temperature. Nevertheless, we believe it is fair to conclude on the basis of the present results that the alkaline-earth fluorides do, in fact, display intrinsic multiphonon absorption over an extended frequency and temperature range. In particular, we find that the absorption is relatively structureless and displays a nearly exponential frequency dependence over most of the range investigated. The temperature dependence is close to the Bose-Einstein form  $\{[n(\omega_0) + 1]^{-\omega/\omega_0}\}$  with  $\omega_0 \sim \omega_B$ .

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