PHYSICAL REVIEW B VOLUME 3, NUMBER 8 15 APRIL 1971

COMMENTS AND ADDENDA

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Temperature Dependence of the NaI:NaCl Resonant Mode System*

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(Received 26 October 1970)

Unusual temperature dependence of the low-lying resonant mode in NaI : NaCl has been measured; the frequency of the absorption line increases with increasing temperature. This is explained semiquantitatively by a model which considers the impurity ion moving in a static anharmonic potential.

The temperature dependence of resonant modes can provide useful information on the anharmonicity of the impurity-host binding forces.[1] Large changes in the absorption strength and centroid frequency of the impurity-induced absorption in the NaI:NaCl system[2] have been observed as the crystal temperature is increased from 1.4 °K. The changes can be analyzed in terms of a harmonic oscillator perturbed by quartic terms. We find that we observe the higher transitions of the oscillator (besides the $0 \rightarrow 1$ transition) as the temperature is raised. This is the first observation of higher transitions in an alkali-halide lattice-defect system, although the $1 \rightarrow 2$ transition has been identified in MnF_2 doped with Eu.[1]

The far-infrared absorption measurements were made using a modified R. I. I. C. LR-100 lamellar interferometer[3] operating aperiodically and a He^3-cooled bolometer detector[4]; instrumental resolution was $\gtrsim 0.23\,cm^{-1}$. The NaI single-crystal[5] samples were doped with 0.4 mole% $NaCl^{27}$. They were mounted on a rotatable sample ring so that their transmission spectra could be compared with the spectrum of pure NaI and the Cl^--induced absorption directly determined. The sample ring could be thermally coupled to the helium bath by a small amount of He^4 exchange gas. The bolometer section of the cryostat was found to be completely thermally isolated from the sample section so that bolometer response was independent of sample temperature. Temperature was varied from 1.4 to 26 °K by a resistance bridge[6] using a calibrated $\frac{1}{8}$-W 100-Ω carbon resistor in contact with the sample ring as the sensor; the heater was a length of manganin wire wound around the sample ring.

Impurity-induced absorption at three temperatures is shown in Fig. 1. When determining absorption strength and centroid frequency, 0.47-cm^{-1} resolution was used to reduce noise and hence reduce uncertainty in the base line. As the temperature is increased, the line appears to broaden on the high-frequency side and then shift to higher

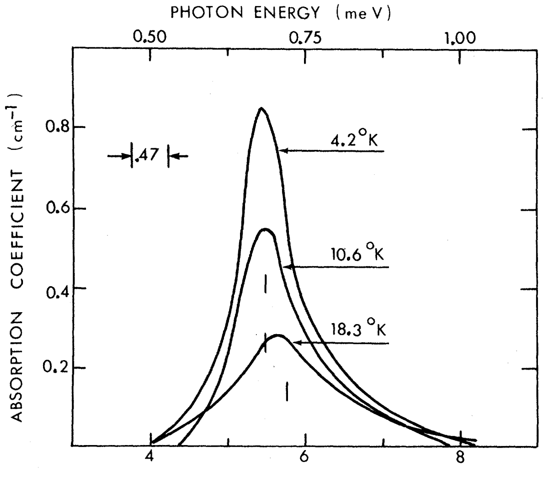

FIG. 1. Temperature dependence of the far-infrared absorption in NaI : $NaCl^{37}$. Instrumental resolution is indicated by the arrows and centroid locations are shown. Impurity concentration is 0.25 ± 0.05 mole%.

frequency and broaden more as the temperature is increased further; at 26 °K the line is centered at $6.0\pm0.5\,\mathrm{cm}^{-1}$. The measured absorption strength decreases with increasing temperature; absorption strength and centroid frequency temperature dependences are summarized in Fig. 2. The observed linewidth (at 0.23-cm^{-1} resolution) increases from 0.3 to about $1\,\mathrm{cm}^{-1}$ over the same temperature range.

Several anharmonic effects have been discussed in the analysis of the temperature dependence of resonant mode systems.[1,7] Two mechanisms can cause a shift of the $0\rightarrow1$ transition energy: dynamic coupling to host lattice phonons and simple thermal expansion. Both of these produce small negative shifts of the mode frequency, i.e., shifts to lower transition energies. The absorption band in NaI: NaCl shifts distinctly to higher transition energy as the temperature is increased. We must therefore look elsewhere to fully explain our experimental results.

The model we propose is a three-dimensional harmonic oscillator perturbed by the potential produced by the crystal field:

$$V(r)=\tfrac{1}{2}m\omega^2r^2+B(x^4+y^4+x^4)+C(x^2y^2+y^2z^2+z^2x^2)\ , \qquad (1)$$

to fourth order in displacement.[8] Isotope-shift measurements[2] indicate that m should set equal to the impurity mass. This model predicts that certain of the $\tfrac{1}{2}(n+1)(n+2)$-fold degenerate harmonic-oscillator states will be split, and that all allowed transitions except the $n=0$ ground state (A_{1g}) to $n=1$ first excited state (T_{1u}) transition will therefore be multiplets. Keeping this fact in mind, we can extract the essential features of the temperature dependence of the system from the more tractable one-dimensional anharmonic oscillator where the unperturbed levels are nondegenerate, and

$$E_{n+1}-E_n=\hbar\omega+3B(\hbar/m\omega)^2(n+1) \qquad (2)$$

is the transition energy between levels n and $n+1$. If we assume that the anharmonicity is small enough so that we can use the harmonic-oscillator partition function, we find the strength for this transition is

$$I(T)/I_0(0)=(e^{-\beta E_n}-e^{-\beta E_{n+1}})/\sum_{n=0}^{\infty}e^{-\beta E_n}\ , \quad \beta=(kT)^{-1} \qquad (3)$$

where $I_0(0)$ is the strength of the $0\rightarrow1$ transition at $T=0$. The second term accounts for spontaneous emission from level $n+1$.

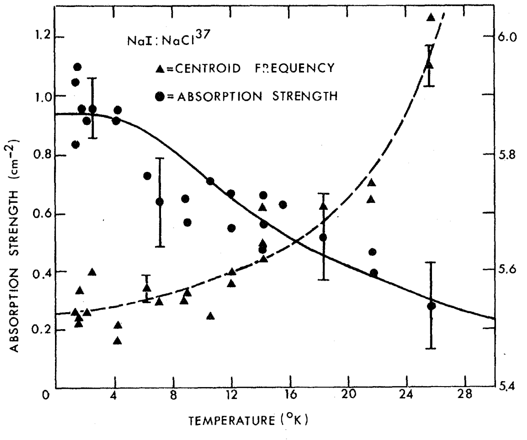

FIG. 2. Temperature dependences of the absorption strength and centroid frequency. The solid curve is the sum of the strengths of the three lowest anharmonic-oscillator transitions calculated from Eq. (3); the dashed curve is a fit to the experimentally determined centroid frequencies.

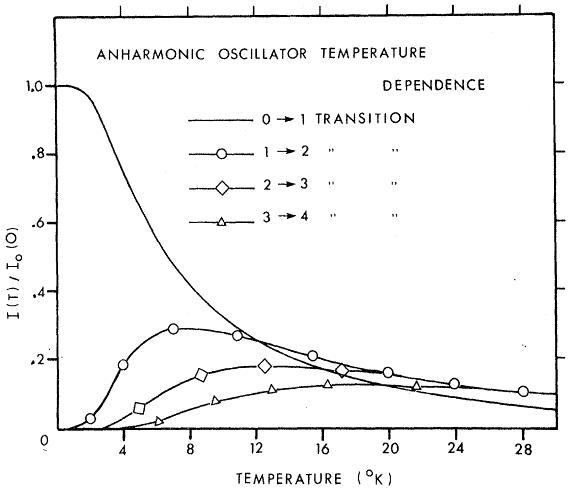

FIG. 3. Calculated temperature dependence of the strengths of the four lowest transitions of a one-dimensional anharmonic oscillator for $B=4.3\times10^{32}\ \mathrm{cm}^{-1}/\mathrm{cm}^4$ in Eq. (3).

We see first from Eq. (2) that if $B>1$, the transitions between excited states all occur at higher frequencies than the $0\rightarrow1$ transition. Equation (3) shows that at low temperatures the $0\rightarrow1$ transition dominates the observed spectrum, but as the temperature is increased, the populations of the excited states increase quickly and transitions between excited states begin to dominate. This is illustrated in Fig. 3 where we plot Eq. (3) for several of the lowest transitions. We see then that we may interpret the upward shift of the absorption frequency as the emergence to dominance of transitions between excited states. The increase in transition energy for these higher transitions is large enough to overcome the effect of thermal expansion and of dynamic coupling to host phonons (both of which cause frequency shifts of all the lines in the opposite direction) and produce the observed shift.

Accurate determination of the excited-state transition energies from these data is not possible. The magnitudes of the two effects which cause a negative shift in energy are not known exactly. In addition, the linewidth is increased due to (i) the multiplet nature of transitions, and (ii) the decreased lifetimes of all states at elevated temperatures. This prevents resolution of the separate transitions. It also prevents very accurate determinations of absorption strengths because of the uncertainty in establishing a base line for such broad lines.

We may however test the consistency of these temperature data with the results of previous work on this lattice-defect combination. We use the anharmonicity parameter $B = 4.3\times10^{32}\,\mathrm{cm}^{-1}/\mathrm{cm}^4$ determined by Stark effect measurements[9,10] (and confirmed by isotope shift determinations[2]) in Eqs. (2) and (3) to predict the total strength of the absorption line. As shown in Fig. 2, an adequate fit to the data is obtained by including only the lowest three transitions in the sum. Including only the lowest few transitions in the sum is reasonable because the increasing width of the higher transitions makes them indistinguishable from background noise. The three lowest transition energies of the one-dimensional oscillator for this choice of B are 5.5, 5.9, and $6.3\,\mathrm{cm}^{-1}$.

It is not possible to extend this procedure to describe quantitatively the magnitude of the observed frequency shift. To attempt to do so would require assumptions about the line shapes of the individual transitions and their temperature dependences, and about the magnitudes of the negative frequency shifts due to dynamic interactions with host lattice phonons. Not enough is known about these systems to allow such assumptions to be made with confidence.

From the analysis of the line-strength data and from the observed magnitude and direction of the frequency shift, we may conclude that the temperature dependence of the NaI:NaCl resonant mode is due to the superposition of allowed transitions between the several low-lying states of an anharmonic oscillator. The temperature dependence of the relative strengths of the transitions is explicable on the basis of thermal population effects. This relatively simple explanation of the temperature dependence has been found to not be applicable for other alkali-halide resonant mode systems studied[1]: KBr:LiBr, NaCl:CuCl, and KI:AgI. In these cases, the $0\rightarrow1$ transition energy is around $20\,\mathrm{cm}^{-1}$, where the density of host phonon states is an order of magnitude greater than at $5.5\,\mathrm{cm}^{-1}$. It is not surprising then that, unlike the NaI:NaCl system, the temperature dependence of these other cases cannot be explained by neglecting the effect of interactions with the host phonons.

The author acknowledges helpful discussions with Dr. R. W. Alexander, Jr. and Dr. A. J. Sievers, and technical assistance from T. Templeton.

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*Work supported by the National Research Council, the Research Corporation, and an S. F. U. President's Research Grant.

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[3] The modification consists of a rotatable motor mount to allow positioning at the zero phase point.

[4] The cryostat housing both samples and detector is similar to that described in Ref. 10.

[5] The doped crystals were grown by the Kryopoulos technique in the Crystal Growing Facility of the Materials Science Center at Cornell University.

[6] Oxford Instruments Ltd. resistance thermometer bridge.

[7] M. V. Klein, *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), Chap. 7.

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