

Benneman, in *Superconductivity in d- and f-Band Metals*, AIP Conference Proceedings No. 4, edited by D. H. Douglass (American Institute of Physics, New York, 1972), pp. 255-292] and  $\mu^* = 0.018$  [L. F. Lou and W. J. Tomasch, Phys. Rev. Lett. **29**, 858 (1972)], we constructed the corresponding curve of  $k_B N(E_F) \Delta T_c / n$  versus Th concentration and compared the latter with the MHZ theoretical curve of  $k_B N(E_F) \Delta T_c / n$  versus  $T_K / T_{c0}$

as explained in the text. The only effect of this procedure was to modify the scaling factor to the respective values of 0.80 and 0.87; the  $T_K$  values remained *unchanged* within the accuracy of the experiment. We also remark that the LaCe  $T_K$  value of 1.1°K determined here is somewhat larger than previous estimates which range from  $\sim 0.1$  to  $\sim 0.6^\circ\text{K}$  (Ref. 6).

<sup>19</sup>J. R. Schrieffer, J. Appl. Phys. **38**, 1143 (1967).

## Multiphonon Absorption in NaF

Dieter W. Pohl and Peter F. Meier\*

IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

(Received 15 November 1973)

The infrared absorption in NaF at the two CO<sub>2</sub> laser wavelengths 10.6 and 9.3  $\mu\text{m}$  was measured between 4 and 400 K. The results complement the previously measured absorption for higher temperatures, and allow for a detailed comparison with theoretical predictions. The experimental temperature dependence at 10.6  $\mu\text{m}$  can be excellently fitted by a curve expected for three-phonon processes in the whole temperature range; the absorption at 9.3  $\mu\text{m}$  fits a mixture of three- and four-phonon processes.

Considerable attention has recently been focused on infrared absorption in alkali halides,<sup>1-10</sup> partially stimulated by the need for lossless windows for infrared lasers (5 to 20  $\mu\text{m}$ ).<sup>11</sup> In this frequency region, the multiphonon absorption caused by lattice anharmonicities dominates the loss mechanisms due to higher-order dipole moments. The temperature dependence of the intrinsic absorption is then characteristic of the number of phonons into which the virtually excited fundamental mode decays. In the temperature interval between 300 K and the melting point, the 10.6- $\mu\text{m}$  absorption was recently investigated by Harrington and Hass<sup>5</sup> (HH). The clearest results were obtained for NaF and NaCl which show a relatively strong absorption. Analyzing their data, HH reported serious discrepancies between the theoretical predictions and their experimental results. The failure of the theory was ascribed to the neglect of the temperature dependence of the phonon frequencies and the transition matrix elements. This gave rise to a series of theoretical approaches<sup>3, 6-9</sup> which took into account the thermal expansion and temperature renormalization of phonon frequencies.

In the course of preparing a forced-Rayleigh-scattering experiment in NaF,<sup>12</sup> we studied the absorption at two CO<sub>2</sub> laser wavelengths (10.6 and 9.3  $\mu\text{m}$ ), and with two samples of different purity. Both crystals were made from Merck "Suprapur" NaF. Sample No. 1 was grown by

standard techniques, with access of air<sup>13</sup>; sample No. 2 was grown in an argon atmosphere.<sup>14</sup> Thus the major difference between the two crystals is the amount of oxygen-containing impurities.

The absorption was measured between 4.2 and 400 K, which favorably complements the data of HH. The following results were obtained: (1) The absorption of the two samples differs by 0.25  $\text{cm}^{-1}$  at 10.6  $\mu\text{m}$  and by 0.30  $\text{cm}^{-1}$  at 9.3  $\mu\text{m}$ , almost independent of temperature. The difference is obviously caused by the different content of impurities. It is of the same order of magnitude as the total absorption and considerably masks the intrinsic temperature dependence. (2) Up to about 90 K, the absorption is almost constant, yielding the values  $\alpha_0(10.6 \mu\text{m}) = 0.27 \pm 0.02 \text{ cm}^{-1}$  and  $\alpha_0(9.3 \mu\text{m}) = 0.12 \pm 0.02 \text{ cm}^{-1}$  for sample No. 2. (3) Between 300 and 400 K, the 10.6- $\mu\text{m}$  absorption of sample No. 1 is slightly larger, and that of sample No. 2 slightly smaller, than the one reported by HH. The almost constant difference  $\Delta\alpha = 0.09 \text{ cm}^{-1}$  between HH's data and those from sample No. 2 might also result from impurities. However, because of a considerably larger total absorption at  $T > 300 \text{ K}$ , the difference is insignificant for the theoretical interpretation.

In Fig. 1, the 10.6- $\mu\text{m}$  experimental absorption of sample No. 2 is plotted together with HH's data on NaF. A log-log plot is required to present the whole temperature and absorption interval. The

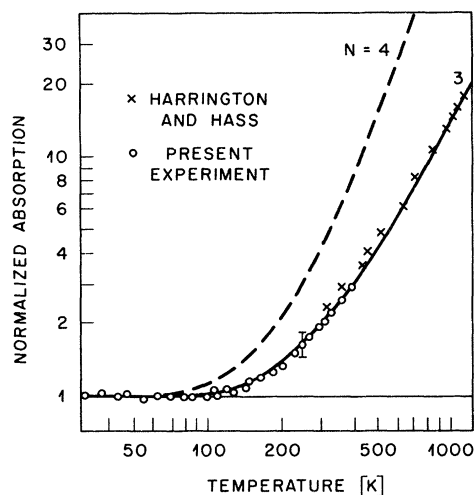


FIG. 1. Experimental and calculated absorption at  $10.6 \mu\text{m}$  versus temperature.

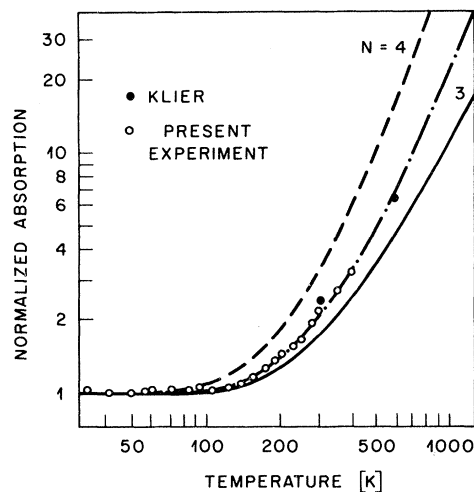


FIG. 2. Experimental and calculated absorption at  $9.3 \mu\text{m}$  versus temperature.

absorption is normalized to  $T=0$ . A smooth set of data is obtained with only a small step in the overlapping zone at 300 to 400 K caused by the above-mentioned difference  $\Delta\alpha$ .

The normalized  $9.3\text{-}\mu\text{m}$  absorption is presented in Fig. 2, together with two data points taken from Klier.<sup>15</sup> Three temperature regimes can clearly be distinguished in both experimental curves: the constant low-temperature absorption indicating negligible occupation of phonon levels, the increase near room temperature due to a

rising phonon population, and the power-law (straight) increase at  $T > T_{\text{Debye}}$ . Because of the large temperature interval covered, the experimental data at  $10.6 \mu\text{m}$  lend themselves particularly well to a comparison with theory.

We consider the absorption  $\alpha_N$  of light with frequency  $\Omega$  above the *Reststrahl* region due to an  $N$ -phonon summation process. In this case, a virtual excitation of the fundamental mode  $f$  decays into  $N$  phonons with energies  $\omega_1, \omega_2, \dots, \omega_N$ . The absorption is then proportional to<sup>16</sup>

$$\alpha_N \propto \sum_{k_1, \dots, k_N} |V^{(N+1)}(0, f; k_1; \dots; k_N)|^2 \delta(\Omega - \omega_1 - \dots - \omega_N) \{ [n(\omega_1) + 1] \cdots [n(\omega_N) + 1] - n(\omega_1) \cdots n(\omega_N) \}, \quad (1)$$

where

$$n(\omega_i) = [\exp(\hbar \omega_i / k_B T) - 1]^{-1}. \quad (2)$$

Here,  $k_i$  denotes both wave vector and polarization.  $V^{(N+1)}$  is essentially the Fourier transform of the derivative of order  $N+1$  of the potential energy with respect to elongations. The form of  $V^{(N+1)}$  implies momentum conservation modulo reciprocal-lattice vectors  $\vec{K}$  ( $\vec{k}_1 + \dots + \vec{k}_N = \vec{K}$ ). The values of  $\omega_1, \dots, \omega_N$  are temperature dependent, but energy conservation requires that their sum be constant.

Hardy and Agrawal<sup>2</sup> pointed out that if all final-state-phonon energies are assumed to be equal ( $\omega_1 = \dots = \omega_N = \Omega/N$ ) and  $V^{(N+1)}$  temperature independent, the following temperature dependence results from Eq. (1):

$$\alpha_N(T) = \alpha_0 \{ [n(\Omega/N) + 1]^N - [n(\Omega/N)]^N \}, \quad (3)$$

where  $\alpha_0$  is the absorption at absolute zero.

Most previous experimental studies had focused on wavelength regions with relatively large absorption, which are readily accessible to classical spectroscopy, but where two-phonon processes dominate. It was not clear, therefore, whether prediction (3) would also account for higher-order processes or whether a more elaborate theory would be required. HH's results, in fact, seemed to favor the second alternative. Bendow,<sup>3</sup> Sparks and Sham,<sup>6</sup> Maradudin and Mills,<sup>7</sup> McGill and Winston,<sup>8</sup> and Rosenstock<sup>9</sup> recently presented such extended theoretical approaches. The original scope of the work of Sparks and Sham<sup>1</sup> and of Mills and Maradudin<sup>4</sup> was to explain the frequency dependence of the absorption. These theories were extended by taking into account thermal expansion and temperature-dependent fre-

quencies, which led to agreement with the results of HH.

In the subsequent analysis we shall demonstrate that the experimental absorption can be explained also in terms of the simple Eq. (3) if, according to the known phonon spectrum,<sup>17</sup> the most probable decay processes are considered. In this way we arrive at perfect agreement for the temperature dependence from 4.2 K up to the melting point. This result indicates that the influence of the above-mentioned extensions might be less pronounced in NaF than predicted. The temperature dependence of the phonon spectrum, for example, might be masked by a flat characteristic of the relevant part of the multiphonon density of states.

The most important parameter entering the temperature-dependent part of Eq. (1) is the number  $N$  of final-state phonons. Generally, a decay into  $N$  phonons is possible if  $N\omega_{\max} > \Omega$ , where  $\omega_{\max}$  is the maximum phonon frequency. Because of the decrease of the matrix elements  $|V^{(j)}|^2$  with increasing  $j$ , the processes with the smallest possible number  $N$  are expected to dominate all the higher-order processes. Evaluation of Eq. (1) would next require calculation of the  $N$ -phonon density of states. For simplicity, we assume that the largest contribution to the sum in Eq. (1) stems from those final-state phonons which dominate the one-phonon density of states. The latter has pronounced peaks at frequencies corresponding to excitations near symmetry points where the dispersion curve is flat (points  $\Gamma$ ,  $X$ , and  $L$  for the NaCl structure).

Inspection of the phonon dispersion curves of NaF<sup>17</sup> shows that for laser light at both 10.6  $\mu\text{m}$  ( $17.8 \times 10^{13} \text{ sec}^{-1}$ ) and 9.3  $\mu\text{m}$  ( $20.3 \times 10^{13} \text{ sec}^{-1}$ ) three-phonon processes are possible since  $\omega_{\max} \approx 8 \times 10^{13} \text{ sec}^{-1}$ . Moreover, around  $\omega = 6 \times 10^{13} \text{ sec}^{-1}$ , i.e., at one third of the 10.6- $\mu\text{m}$  frequency, the one-phonon density of states is large because of contributions from the LO modes near  $X$  and the LO and LA modes near  $L$ . Thus a decay into three longitudinal phonons with wave vectors near  $\vec{k}_1 = [1, 0, 0]$ ,  $\vec{k}_2 = [-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}]$ , and  $\vec{k}_3 = [-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$  or equivalent values is probable and satisfies the condition of energy conservation for  $\Omega = 17.8 \times 10^{13} \text{ sec}^{-1}$ . Thus we expect that the absorption in NaF at 10.6  $\mu\text{m}$  is dominated by three-phonon processes. The new situation ( $N=3$  instead of 4!)<sup>5</sup> demands re-examination of the theoretical interpretation. The temperature dependence according to Eq. (3) for a three-phonon process, with  $\alpha_0$  normalized to 1, is shown in

Fig. 1 (solid curve) together with the curve expected for four-phonon processes (dashed line). It turns out that agreement between the three-phonon curve and the experimental absorption at 10.6  $\mu\text{m}$  is perfect, while four-phonon processes would require substantial corrections of the type discussed in the extended theories.<sup>3,6-9</sup> It seems rather unlikely, however, that these corrections should result in an apparent three-phonon temperature dependence over the *whole* temperature interval.

The 9.3- $\mu\text{m}$  photon cannot decay into three phonons near symmetry points. Nevertheless, the one-phonon density of states around  $\Omega/3$  is certainly nonvanishing. In view of the above arguments, we expect that the three-phonon absorption is still dominant, but there may be a contribution from four-phonon processes. In Fig. 2, a comparison between experimental and calculated absorption [again using Eq. (3)] is presented. The experimental points, in fact, are located between the curves for  $N=3$  and 4. A good fit to the experimental absorption is obtained with a mixture of 80% three- and 20% four-phonon processes (dash-dotted curve).

The perfect agreement, in particular at 10.6  $\mu\text{m}$ , between the experimental absorption and the results of the simple theoretical expression (3) is surprising, bearing in mind the substantial corrections predicted by the above-mentioned extended theories. The essential simplification of most approaches<sup>3,7-9</sup> was the introduction of a single Einstein oscillator frequency near  $\omega_f$  ( $=\omega_{\text{TO}}$ ). It should be noted, however, that the phonon branches of alkali halides are spread over a relatively large energy interval so that the maximum frequency  $\omega_{\max} = \omega_{\text{LO}}(\vec{k}=\vec{0}) \approx 2\omega_f$ .<sup>17-19</sup> Hence, it is questionable whether the description of the whole phonon spectrum by Einstein oscillators with a single frequency  $\omega_f$  is adequate. The theory of Sparks and Sham<sup>6</sup> is more fundamental, using a Debye spectrum instead. Starting from an assumed two-particle potential and accounting for vertex corrections, these authors evaluate absolute values of the absorption and its frequency dependence. As far as the temperature dependence is concerned, the change of  $\omega_{\max}$  and  $\omega_f$  between 0 and 1000 K amounts to 3 and 10%, respectively.<sup>20</sup> The variation of the three-phonon frequencies contributing to the 10.6- $\mu\text{m}$  absorption will be within the same interval. Because of energy conservation the expression in curly brackets in Eq. (1) is fairly insensitive to such minor variations in  $\omega_i$  ( $i=1, \dots, N$ ). The remain-

ing small effect, moreover, might be masked by the finite lifetime of the phonons involved. The one-phonon density of states therefore is smeared out, and will not show any critical points, but rather broad maxima at the frequencies corresponding to symmetry points.

The temperature dependence of the absorption in KBr, measured by Barker<sup>21</sup> and analyzed in Ref. 6 for  $418\text{ cm}^{-1}$ , is also in quantitative agreement with Eq. (3) for  $N=3$ . The phonon curves of KBr,<sup>18</sup> in fact, indicate that the lowest-order processes at that wave number involve three phonons. In NaCl at  $10.6\text{ }\mu\text{m}$  the lowest-order process involves four phonons.<sup>19</sup> The experimental data of HH can be explained in terms of Eq. (3) if an additional extrinsic absorption  $\alpha_{\text{ex}}$  is assumed. A good fit is obtained with  $\alpha_0=0.0002\text{ cm}^{-1}$ . Such a small extrinsic absorption, caused by a few parts per million of impurities, might well exist even in a good quality crystal. However, the experimental deviation from the simple four-phonon curve might equally well relate to the above-mentioned extension of the basic theory. It would be interesting to repeat the measurements of HH with even purer crystals and at lower temperatures in order to decide this intriguing alternative.

To conclude, the complete temperature dependence of the absorption, in the particular case of NaF at  $10.6\text{ }\mu\text{m}$ , can be described as a pure three-phonon process. The different results from the two samples emphasize the importance of impurities for the small-absorption multiphonon region.

The authors are indebted to V. Irniger and K. Gisler for technical assistance.

\*IBM Postdoctoral Fellow of the Institute for Theoretical Physics, University of Zurich, Zurich, Switzerland.

<sup>1</sup>M. Sparks and L. J. Sham, *Solid State Commun.* **11**, 1451 (1972).

<sup>2</sup>J. R. Hardy and B. S. Agrawal, *Appl. Phys. Lett.* **22**, 236 (1973).

<sup>3</sup>B. Bendow, *Appl. Phys. Lett.* **23**, 133 (1973).

<sup>4</sup>D. L. Mills and A. A. Maradudin, *Phys. Rev. B* **8**, 1617 (1973).

<sup>5</sup>J. A. Harrington and M. Hass, *Phys. Rev. Lett.* **31**, 710 (1973).

<sup>6</sup>M. Sparks and L. J. Sham, *Phys. Rev. Lett.* **31**, 714 (1973), and *Phys. Rev. B* **8**, 3037 (1973).

<sup>7</sup>A. A. Maradudin and D. L. Mills, *Phys. Rev. Lett.* **31**, 718 (1973).

<sup>8</sup>T. C. McGill and H. V. Winston, *Solid State Commun.* **13**, 1459 (1973).

<sup>9</sup>H. B. Rosenstock, *J. Appl. Phys.* **44**, 4473 (1973).

<sup>10</sup>T. Deutsch, to be published.

<sup>11</sup>M. Sparks, *J. Appl. Phys.* **42**, 5029 (1971), and *Appl. Phys. Lett.* **23**, 368 (1973).

<sup>12</sup>D. W. Pohl, S. E. Schwarz, and V. Irniger, *Phys. Rev. Lett.* **31**, 32 (1973).

<sup>13</sup>Supplied by Kark Korth oHG, Kiel, W. Germany.

<sup>14</sup>Supplied by Sonderforschungsbereich 67 an der Universität Stuttgart, Stuttgart, W. Germany.

<sup>15</sup>M. Klier, *Z. Phys.* **150**, 49 (1958).

<sup>16</sup>This formula is obtained by straightforward extension of the usual perturbation theory for  $N=2$ ; see, e.g., R. A. Cowley, *Rep. Progr. Phys.* **31**, 123 (1968).

<sup>17</sup>W. J. L. Buyers, *Phys. Rev.* **153**, 923 (1967).

<sup>18</sup>A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran, *Phys. Rev.* **131**, 1025 (1963).

<sup>19</sup>G. Raunio, L. Almqvist, and R. Stedman, *Phys. Rev.* **178**, 1496 (1969).

<sup>20</sup>I. F. Chang and S. S. Mitra, *Phys. Rev. B* **5**, 4094 (1972).

<sup>21</sup>A. J. Barker, *J. Phys. C: Proc. Phys. Soc., London* **5**, 2276 (1972).

## Conduction-Electron Spin Density around Fe Impurities in Cu above and below $T_K$ \*

James B. Boyce† and Charles P. Slichter

*Materials Research Laboratory and Department of Physics, University of Illinois, Urbana, Illinois 61801*

(Received 7 November 1973)

We have observed the nuclear resonances of five shells of Cu atoms which are near neighbors to single Fe atoms in dilute alloys of  $\text{CuFe}$ , following four shells from 300 K to well below the Kondo temperature, 29 K. The spin density has the same temperature dependence as the magnetic susceptibility, showing that contrary to some speculation there is no drastic change in the spatial polarization associated with the "Kondo condensation."

Considerable effort, both theoretical and experimental, has gone into determining the nature of the ground state of a Kondo system,<sup>1-3</sup> but to

date important questions remain unresolved. The classic Kondo system is a dilute alloy of  $\text{CuFe}$ . Polarization of the Fe by application of an exter-