host to another, since the absorption bands $4f^7 \rightarrow 4f^6 5d$ are at about the same energy and show similar crystal-field splittings in all three hosts.[13] We have made the further observation that the intensities of the impurity-induced spectra scale among these crystals in rough proportion to the intensities of the one- and two-phonon scattering in the pure crystals. This evidence suggests that the f-d transitions may not be of primary importance in determining the change in the local polarizability derivatives as has been assumed in this work.[14]

V. CONCLUSIONS

The primary results of this work has been the demonstration of the inadequacy of the nearest-neighbor coupling model for calculations of impurity-induced phonon spectra even in highly ionic crystals, such as the alkaline-earth fluorides. The apparent success of this model is some of the alkali-halide lattices[1] is possibly due to the more similar anion and cation masses in the host crystals studied in Ref. 1. However, there remains the possibility that the electronic states responsible for the impurity scattering are perturbed band states in the fluorite systems discussed in this paper, whereas they are more localized for Tl^+ in the alkali halides. This is unlikely, since the $6s\,6p$ excited states of the Tl^+ ion, which are most likely the intermediate electronic states responsible for the scattering in the alkali halides,[2] are also not very well localized compared with inter-ion distances. We, therefore, feel that the nearest-neighbor coupling model will not give an accurate representation of the impurity-induced scattering in any but the simplest lattices in which all ions vibrate with roughly equal amplitudes throughout the phonon spectrum.

[†] Research supported by the National Science Foundation.

[*] Alfred P. Sloan Foundation Fellow.

[‡] Present address: Bayer AG, Leverkusen, West Germany.

[1] R. T. Harley, J. B. Page, Jr., and C. T. Walker, Phys. Rev. B **3**, 1365 (1971). This reference contains a brief review of the work in this area up to 1970.

[2] G. Benedek and N. Terzi, in *Proceedings of the Second International Conference on Light Scattering in Solids* (Flammarion, Paris, 1971), p. 291.

[3] D. H. Kuhner, H. V. Lauer, and W. E. Bron, Phys. Rev. B **5**, 4112 (1972).

[4] L. Couture and J. P. Mathieu, Ann. Phys. (N.Y.) **3**, 521 (1948).

[5] R. Loudon, Proc. Roy. Soc. A **275**, 218 (1963); Adv. Phys. **13**, 423 (1964).

[6] E. Loh, Phys. Rev. **175**, 533 (1968).

[7] C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill, New York, 1962).

[8] R. Srivastava, H. V. Lauer, L. L. Chase, and W. E. Bron, Phys. Lett. A **36**, 333 (1971).

[9] W. H. Kleiner, J. Chem. Phys. **20**, 1784 (1952).

[10] R. G. Shulman and S. Sugano, Phys. Rev. Lett. **7**, 157 (1961).

[11] W. E. Bron, D. Kuhner, and A. Man, Bull. Am. Phys. Soc. **17**, 313 (1972).

[12] A. A. Kaplyanski and A. K. Przevusky, Opt. Spektrosk. **19**, 597 (1965) [Opt. Spectrosc. **19**, 331 (1965)].

[13] A. A. Kaplyanski and P. P. Feofilov, Opt. Spektrosk. **13**, 235 (1965) [Opt. Spectry. (USSR) **13**, 129 (1962)].

[14] *Note added in proof:* Recent Raman scattering measurements in BaF_2 containing Ca^{2+} impurities and CaF_2 containing Ba^{2+} impurities show no observable impurity-induced scattering. This suggests that neither perturbed electronic band states nor perturbed phonon eigenvectors contribute measurably to the scattering observed with Eu^{2+} impurities in the work reported here. The decreasing scattering efficiency of Eu^{2+} in the series BaF_2, SrF_2, CaF_2 apparently results from the decrease in the electron-phonon coupling for the $5d$ electron in these hosts. This effect is also apparent in the increase in the absorption strength of the zero-phonon lines of Eu^{2+} in this series (see Ref. 13).

PHYSICAL REVIEW B VOLUME 7, NUMBER 8 15 APRIL 1973

Thermal Conductivity of Cerium Magnesium Nitrate

J. P. Harrison and J. P. Pendrys
Department of Physics, Queen's University, Kingston, Ontario, Canada

(Received 21 September 1972)

The thermal conductivity of cerium magnesium nitrate has been measured over the temperature range 0.2–1.5 °K. When an assumption is made that the surface of the crystal is damaged to a depth of 150 μm by sandblasting, the conductivity measurements are entirely described by the Casimir theory of boundary scattering of phonons.

I. INTRODUCTION

Cerium magnesium nitrate (CMN) is a Kramers salt that has been extensively investigated largely because of its application in low-temperature refrigeration and thermometry. Some years ago it was found that at very low temperatures the thermal relaxation between CMN and He^3 was several orders of magnitude faster than expected either theoretically or empirically if judged by other materials.[1] Subsequent experiments showed that this was a valid physical phenomenon.[2] Later, a theoretical paper confirmed that the enhanced coupling should in fact have been so.[3] It seemed that a quantity of interest would be the Kapitza resistance measured in the usual way, and we have set out to measure this. However, during the course of these experiments, a paper on the thermal conductivity of CMN was published.[4] The conclusion of this work was that even at the lowest temperatures the phonon mean free path in CMN is limited internally by invisible cleavage planes, rather than by the boundaries of the crystal. As our method of measuring Kapitza resistance depended upon a phonon mean free path equal to the size of the crystal, it was important to investigate the size effect of the thermal conductivity of our crystals. As a matter of course it had been confirmed that the crystals had a high conductivity, but the work of Robichaux and Anderson has shown that high thermal conductivity is not necessarily commensurate with phonons traveling across the crystal. In addition, it has recently been proposed that in molecular crystals, the phonon mean free path will never approach crystal dimensions.[5]

II. SAMPLE PREPARATION

The starting material for the samples was obtained from G. Frederick Smith Chemical Co. The crystals were grown by evaporation from saturated solution at 4 °C. They were not uniformly flawless, unlike others described.[4,6] Macroscopically, the crystals exhibited the usual sixfold symmetry, but in all cases the hexagonal crystal showed three clear sections and three cloudy sections. We have no explanation for this curious behavior. However, the three clear sections were indeed very clear optically, and as it had been found that these sections produced samples with liquid-helium-temperature thermal conductivities as high as 3 W $\mathrm{cm}^{-1}\,{}^{\circ}\mathrm{K}^{-1}$, there was little incentive to try for completely flawless crystals.

The samples for the present series of measurements were cut with a string saw from a clear section of a crystal, and then water polished to size. Occasionally a cleave would develop within a sample during polishing. These cleaves were clearly visible under appropriate illumination. Such a sample was rejected.

The samples were sandblasted with 600-μm glass beads to ensure diffuse phonon scattering at the crystal walls.[7,8]

III. METHOD OF MEASUREMENT

The measurement technique was quite standard. Figure 1 shows the sample mounting schematically. The sample holder and lower section of the mixing chamber of a dilution refrigerator were from one piece of copper. The samples was attached to the holder by an indium-faced phosphor-bronze clamp[9] and also by copper foil glued with GE7031 varnish to the lower part of the crystal and to the holder. Mechanically the sample was in antiphase to the rest of the refrigerator, hopefully to reduce vibration. The two sample thermometers were ground-down $\frac{1}{2}$-W matched 100-Ω Speer carbon resistors. They were bonded to the sample with GE7031 varnish. The heater was a 1000-Ω length of nichrome wire wound onto a 1-mm-diam copper rod. The rod in turn was thermally connected to the sample with copper foil and GE7031 varnish. Attached to the outside of the mixing chamber was a 1000-Ω nichrome heater and $\frac{1}{2}$-W 220-Ω Speer carbon resistor; these together with a resistor net, a PAR phase-sensitive detector, and a power amplifier made up a temperature-control circuit.

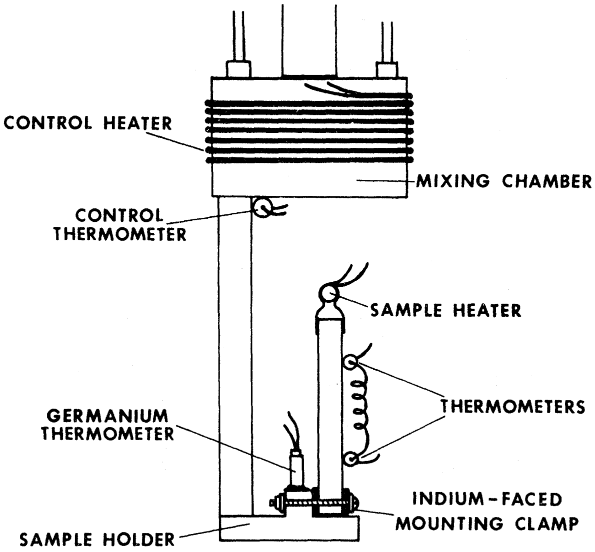

FIG. 1. Schematic diagram of the sample mounted in the sample holder.

The primary thermometer for the experiment was a Solitron SP5401 germanium thermometer that had been calibrated against the vapor pressure of He^3 and the magnetic susceptibility of cerium magnesium nitrate. The low-temperature limit of the experiment was determined by the 0.2 °K low-temperature limit of this thermometer. Measurements were made and the data analyzed by the method described by Seward.[10]

IV. RESULTS

The dimensions of the samples and their thermal conductivities are shown in Fig. 2. In all cases, the heat current was in the basal plane of CMN. The second dimension, the thickness, was in the c direction of the crystal. It can be seen that the thermal conductivity κ for the samples shows a cubic temperature variation. This is brought out more clearly in Fig. 3, which shows κ/T^3 plotted as a function of temperature. An analysis of these curves shows that the conductivity of all four samples can be represented by

$$\kappa \propto T^n, \quad \text{where } n = 3.0 \pm 0.1.$$

V. DISCUSSION OF RESULTS

The first conclusion is that the thermal conductivity of the CMN samples shows the cubic temperature variation expected for boundary scattering of the phonons. Next, we must compare the magnitude with that expected. The results will be compared to the Casimir model for boundary scattering[11] as this has proved successful in the past.[8] Following Casimir, we write the heat flux as

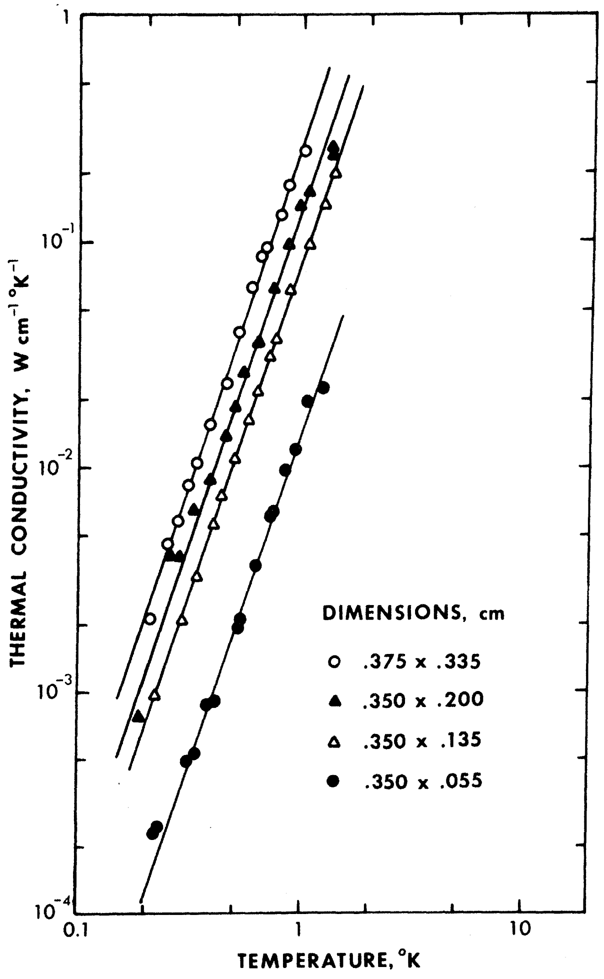

FIG. 2. Thermal conductivity of CMN as a function of temperature. The dimensions shown are the width and thickness of the rectangular samples. The thickness was in the direction of the crystalline c axis. The straight lines have a slope of 3.

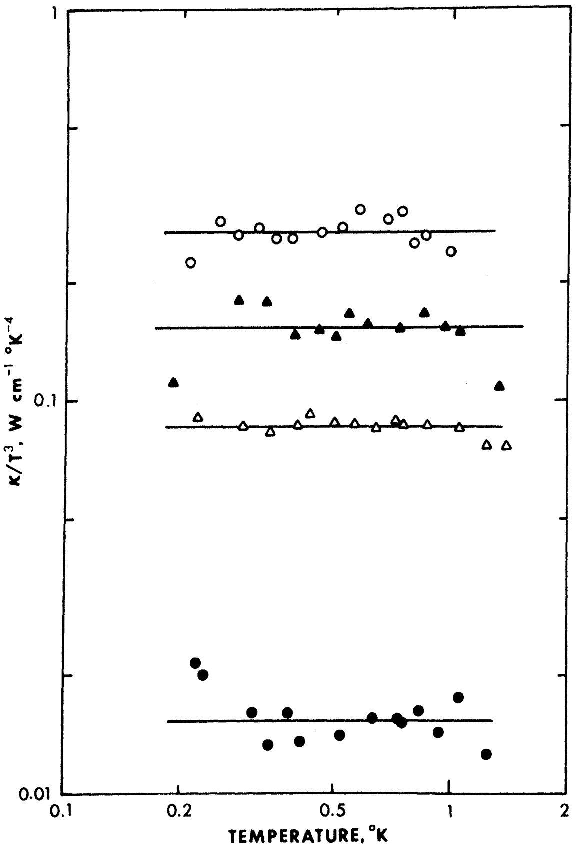

FIG. 3. Plot of κ/T^3 as a function of temperature for the same four samples as shown in Fig. 2.

$$T^3 \frac{4\pi^4 k_B^4}{15h^3} \frac{dT}{dz} \iiiint \frac{z\cos\theta_1 \cos\theta_2 \, d\sigma_1 \, d\sigma_2}{r_{12}^2} \sum_{i=1}^{3} \frac{1}{v_i^2},$$

where $d\sigma_1$ and $d\sigma_2$ are, respectively, increments of a cross section of the sample and of the surface of the sample, r_{12} is the distance between $d\sigma_1$ and $d\sigma_2$, and θ_1 and θ_2 are the angles between r_{12} and the normals to $d\sigma_1$ and $d\sigma_2$. v_i is the velocity of the ith phonon mode, which is in general a function of angle, and z is the axial direction of the sample. Now, it happens that the sound velocity in lanthanum magnesium nitrate, and so presumably also in cerium magnesium nitrate, is quite isotropic.[12] Thus, the velocity term can be taken out of the integral, and an analytic solution obtained for a long rectangular crystal. The expression for the thermal conductivity in terms of the heat capacity becomes

$$\kappa = \tfrac{1}{3} C_v \, \bar{v} \, l,$$

where

$$\bar{v} = \sum v_i^{-2} \Big/ \sum v_i^{-3}, \quad l = 1.115 a f(x),$$

$$f(x) = \frac{1}{4.46}\left(\frac{1+x^3}{x} - \frac{(1+x^2)^{3/2}}{x} \right.$$

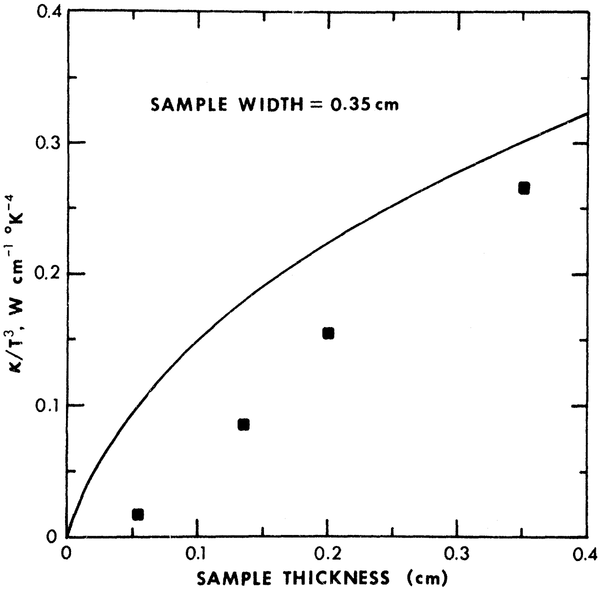

FIG. 4. Mean values of κ/T^3 shown as a function of sample thickness. The solid line is the variation expected from the Casimir model of boundary scattering. We note that there is an empirical fit to the data of $\kappa/T^3 = 0.88\ (t - 0.035)$ W cm^{-1} °K^{-4}, where t is the thickness of the crystal in cm.

$$+\frac{3x}{2}\ln\frac{(1+x^2)^{1/2}+1}{(1+x^2)^{1/2}-1}+\frac{3}{2}\ln\frac{(1+x^2)^{1/2}+x}{(1+x^2)^{1/2}-x}\Bigg) .$$

a is the width of the sample and x is the ratio of thickness to width.

We note that in the region of $x = 1$, $f(x) \sim (1+x)/2$ and over the range $0 < x < 1$, $f(x)$ can be well approximated by $x^{0.6}$; this is close to the $x^{0.5}$ dependence one might naively expect.

For CMN, the Debye temperature has been determined from heat-capacity measurements as 61.5 °K in the low-temperature limit.[13] The sound velocities are given by[12,14]

$$v_{\text{long}} = 3.65\times10^5 \text{ cm sec}^{-1},$$

$$v_{\text{trans}} = 2.08\times10^5 \text{ cm sec}^{-1},$$

$$v_{\text{trans}} = 1.92\times10^5 \text{ cm sec}^{-1} .$$

Thus

$$C_v = 1.10\times10^{-5}\,T^3 \text{ J cm}^{-3}\,{}^\circ\text{K}^{-1}$$

and

$$\bar{v} = 2.12\times10^5 \text{ cm sec}^{-1} .$$

As has been noted by McBride, the Debye temperatures determined from heat capacity and from sound velocities are identical. Substituting into the expression for κ, we obtain

$$\kappa = 0.867T^3 a f(x) \text{ W cm}^{-1}\,{}^\circ\text{K}^{-1} .$$

In Fig. 4, we compare the experimental determination for κ/T^3 for the four samples with this predicted expression. Note that the point for the largest sample has been plotted as if the dimensions were 0.350×0.360 cm instead of the actual 0.375×0.335 cm. That is, the thickness was adjusted up for this slightly wider sample so that all four could be represented on a single plot of κ/T^3 as a function of sample thickness. While the experimental values are about the correct magnitude, in all cases they are low. We have interpreted this deviation as due to a damaged surface layer of the crystal. This after all was the purpose of sandblasting the surface. Figure 5 shows the comparison of the experimental results with the Casimir theory on the assumption that all surfaces of all samples have a 150-μm layer with zero conductivity. There is seen to be good agreement. The 150-μm layer of damage is not unreasonable in view of the 600-μm glass beads used for sandblasting.

VI. CONCLUSION

The measurements show that the Casimir theory of boundary scattering is valid to describe the low-temperature thermal conductivity of cerium magnesium nitrate. In addition, it is clear that even in such a complex structure as crystalline cerium

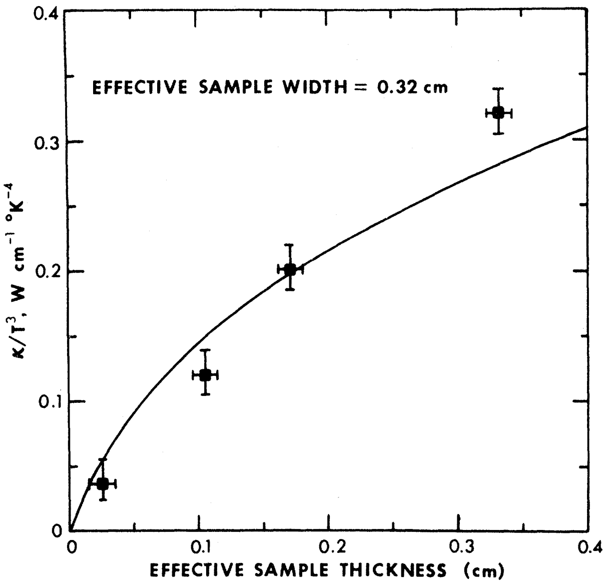

FIG. 5. Mean values of κ/T^3 shown as a function of effective sample thickness. A damaged layer of 150-μm depth is assumed on all sample surfaces. The error bars correspond to 150 ± 50-μm depth. The solid line is the variation expected from the Casimir model of boundary scattering. Note that the expected conductivity is slightly lower due to the lower effective width of the samples, and that the conductivity values are higher due to the lower effective cross-sectional area.

magnesium nitrate, the phonon mean free path can be at least as long as 3.5 mm. Further support of this conclusion is given by recent heat-pulse-propagation experiments which clearly show ballistic-phonon propagation across 5-mm samples. This work will be described elsewhere.

ACKNOWLEDGMENTS

We thank Dr. S. McBride for discussion concerning the velocity of sound in cerium magnesium nitrate and lanthanum magnesium nitrate. The financial support of the National Research Council is gratefully acknowledged.

---

[1] W. R. Abel, A. C. Anderson, W. C. Black, and J. C. Wheatley, Phys. Rev. Lett. **16**, 273 (1966).

[2] W. C. Black, A. C. Mota, J. C. Wheatley, J. H. Bishop, and P. M. Brewster, J. Low Temp. Phys. **4**, 391 (1971); M. P. Bertinat, D. F. Brewer, and J. P. Harrison, J. Low Temp. Phys. **2**, 157 (1970).

[3] A. J. Leggett and M. Vuorio, J. Low Temp. Phys. **3**, 359 (1970).

[4] J. E. Robichaux and A. C. Anderson, Phys. Rev. B **2**, 5035 (1970).

[5] J. N. Haasbroek, in International Conference on Phonon Scattering in Solids, Paris, 1972 (unpublished).

[6] R. A. Fisher, Rev. Sci. Instrum. **43**, 386 (1972).

[7] R. O. Pohl, Phys. Rev. **118**, 1499 (1960).

[8] P. D. Thacher, Phys. Rev. **156**, 975 (1967).

[9] See, for instance, M. V. Klein, and R. F. Caldwell, Rev. Sci. Instrum. **37**, 1291 (1966).

[10] W. D. Seward, Ph.D. thesis (Cornell University, 1965) (unpublished); Materials Science Center Report No. 368 (unpublished).

[11] H. B. G. Casimir, Physica (The Hague) **5**, 495 (1938). Note that on p. 497 of this paper, the second equation should contain $8\pi/3$ instead of $4\pi^2/3$. See also P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).

[12] S. L. McBride (private communication).

[13] C. A. Bailey, Proc. Phys. Soc. Lond. **83**, 369 (1964).

[14] The method of measurement is described by T. H. Chou, S. L. McBride, and N. Rumin, Can. J. Phys. **49**, 1597 (1971).

PHYSICAL REVIEW B VOLUME 7, NUMBER 8 15 APRIL 1973

Lattice Dynamics of Ionic Microcrystals

T. P. Martin
Max Planck Institut für Festkörperforschung, 7 Stuttgart, Germany

(Received 25 October 1972)

The density of phonon states and infrared absorption of RbF microcrystals have been calculated using a rigid-ion model. The microcrystals were assumed to be rectangular solids containing up to 144 atoms. The density of states of the microcrystals, although shifted to lower frequency, was found to have the same shape as the density of states assuming cyclic boundary conditions. The fundamental infrared absorption could be characterized as three distinct bands due to edge modes, surface modes, and volume modes. These absorption bands split in crystals with noncubic shape, in surprisingly good agreement with a continuum theory. In addition to the fundamental absorption, the calculation displayed a weak low-frequency absorption which resembled the density of states.

I. INTRODUCTION

Considerable attention has been given to the macroscopic phonon properties of finite crystals.[1] An important macroscopic effect in small polar crystals is a shift in the optically active modes of vibration due to surface polarization. This macroscopic effect can be calculated using a continuum model of the crystal, i.e., by applying the appropriate electromagnetic boundary conditions to a material described by a frequency-dependent complex dielectric function. With the inclusion of retardation, the continuum model can be applied to crystals of arbitrary size. Polariton modes localized at a plane surface have been predicted by this model[2,3] and have been observed experimentally.[4,5] Although many surface effects have been successfully explained by the continuum model, it has distinct limitations. The model contains only one characteristic frequency, the pole of the dielectric function, which describes the crystal. Clearly, such a model cannot be expected to describe effects which are dependent on the structure of the phonon density of states. In addition, the continuum model cannot be used for modes so highly localized that the crystal's atomicity is important.

Less attention has been given to the microscopic phonon properties of a finite crystal, that is, those properties that depend on the perturbed nature of the atomic layers at the surface. One reason for this lack of attention is that the continuum model is not appropriate to predict microscopic effects. An alternative approach, which is appropriate, is a lattice-dynamical calculation which considers the finite crystal to be a large molecule. Such a calculation has the advantage that it contains a microscopic description of the