Optical Constants of Potassium Bromide in the Far Infrared

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One of the fruits of the recent developments in far-infrared techniques has been the knowledge of the whole vibrational spectrum of a solid and its evolution with temperature. We consider here the particular case of potassium bromide, which has been studied elsewhere by neutron diffraction, and we give all the information obtained in the laboratory by the different methods of far-infrared spectrometry now available: (1) the reflectivity of potassium bromide at liquid-helium, liquid-nitrogen, and room temperature, including the effect of polarization, grazing incidence, and the quality of the surface, and interpreted according to a Kramers-Kronig analysis and a Lorentz analysis with two linear damped oscillators; (2) the transmission of thin layers at normal and oblique incidence, and a determination of the complex index of refraction, the compressibility coefficient, and the effective charge of the ions; (3) the very-far-infrared transmission of thick samples and its temperature dependence explained by phonon-difference processes; and (4) the first spectroscopic observation of the phonon spectrum of an ionic crystal, provided by sodium-induced absorption in potassium bromide, with peaks at 101, 83.5, and 71.5 cm^{-1}, having the same frequencies as the three maxima in the lattice-mode density, which correspond approximately to characteristic TO, LA, and TA phonons. The effect of other impurities and of neutron irradiation is also considered.

I. INTRODUCTION

THE optical constants of potassium bromide have still hardly been studied in the far infrared. The transmission of a thin plate at room temperature has been known since 1932, when Barnes located the minimum of transmission at 113 cm^{-1}.[1] This position has been approximately located again by Boccarra[2] at 113.2 cm^{-1}, by Martin[3] at 115.8 cm^{-1} and by Wilkinson[4] at 112 cm^{-1}; Wilkinson also determined the position of the band at liquid-nitrogen temperature: 121 cm^{-1}. Martin's measurements[3] concerning the transmission of thin layers of alkali halides at liquid-helium temperature do not concern potassium bromide, and there exists information only about the very far infrared and for very thick plates.[5,6] Recently, however, Martin[7] did study a thin KBr layer at liquid-helium temperature and found the band at 120.3 cm^{-1}. The reflectivity of a thick plate at room temperature has been known since Czerny and Roder, in 1938, found a maximum without any structure at nearly 83 μ. This spectrum is confirmed by Yoshinaga[8] for an incidence of 12°; however, for an incidence of 52°, a secondary maximum appears at nearly 58 μ. We should also mention the work of Martin,[3] who found a secondary maximum at nearly 72 μ (139 cm^{-1}) but insisted upon the importance of having the surface well polished. There have been no reflection measurements at low temperature. This lack is unfortunate for KBr, since in that case we have precise information about phonons from neutron diffraction.[9] In Table I are tabulated the frequencies of some characteristic phonons at 90°K.

II. REFLECTION SPECTRA UNDER QUASINORMAL INCIDENCE

A. Experimental

All spectra have been obtained with a grating spectrometer[10] specially built in the laboratory to give the reflectivity of crystals at low temperatures. The sample is cut into a prism (Fig. 1) to avoid interference. The value of the angle of incidence is 15°. Figure 2 gives the reflectivity at three temperatures. A weak secondary maximum appears at 60 μ for room temperature, in agreement with Yoshinaga's experiment.[8] The principal maximum increases in intensity and moves to high frequencies when the temperature decreases. The reflectivity is close to zero at 50 μ. The integrated reflectivity $\int R(\lambda)d\lambda$, or $\int R(\nu)d\nu$, increases when T decreases. The data of Fig. 2 are perceptibly modified
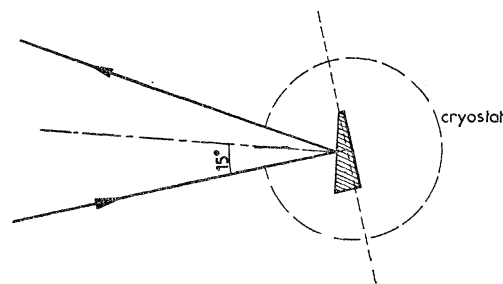

FIG. 1. The KBr plate is cut into a prism to give directly the true reflectivity R^*.

[1] R. B. Barnes, Z. Physik, **75**, 723 (1932).
[2] N. Boccarra, J. Phys. Radium **23**, 287 (1962).
[3] G. O. Jones, D. H. Martin, P. A. Mawer, and C. H. Perry, Proc. Roy. Soc. (London) **A261** 10 (1961).
[4] G. R. Wilkinson, in *Infrared Spectroscopy and Molecular Structure* edited by Mansel Davies (American Elsevier Publishing Company, Inc., New York, 1965), Chap. III, p. 85.
[5] R. H. Stolen, thesis, University of California, Berkeley, 1963 (unpublished).
[6] A. Hadni, P. Henry, J.-P. Lambert, G. Morlot, P. Strimer, and D. Chanal, J. Phys. Suppl. **28**, 118 (1967).
[7] D. H. Martin, Phil. Mag. Suppl. **14**, 39 (1965).
[8] A. Mitsuishi, Y. Yamada, and H. Yoshinaga, J. Opt. Soc. Am. **52**, 14 (1962).
[9] A. D. B. Woods *et al.*, Phys. Rev. **131**, 1025 (1963).
[10] A. Hadni, Ann. Phys. (Paris) **9**, 9 (1964).

by the quality of the surface and the polarization of the incident radiation.

When the incidence is no longer normal, we know from Fresnel's formulas that the p component, with the E vector in the plane of incidence, is not so well reflected as the s component. However, the effect is small and, for instance, in the case of NaCl, Yoshinaga has not seen any difference for $i = 12°$.[8] In the case of KBr, for $i = 15°$, it seems that the p component is the more strongly reflected. Of course, this could not be explained by Fresnel's formulas, which we have used to get Fig. 3, with $i = 15°$ and the values of n and k given by Figs. 11 and 12:

$$R_s = \frac{(a - \cos i)^2 + b^2}{(a + \cos i)^2 + b^2}, \tag{1}$$

$$R_p = R_s \frac{(a - \sin i \tan i)^2 + b^2}{(a + \sin i \tan i)^2 + b^2}, \tag{2}$$

with

$$2a^2 = [(\epsilon' - \sin^2 i)^2 + \epsilon''^2]^{1/2} + (\epsilon' - \sin^2 i),$$

$$2b^2 = [(\epsilon' - \sin^2 i)^2 + \epsilon''^2]^{1/2} - (\epsilon' - \sin^2 i),$$

and

$$\epsilon' = n^2 - k^2, \tag{3}$$

$$\epsilon'' = 2nk. \tag{4}$$

We see in Fig. 3 that both R_s and R_p should cancel at the minimum of reflectivity; and that R_s is slightly larger than R_p, as Yoshinaga's experiments showed for NaCl, and as has also checked in our laboratory for NaCl.

The reproducibility of our reflectivity measurements is often $\pm 2\%$ and, within this accuracy, the quality of the surface has no importance, except at the peak, where the reflectivity varies (for example) from 65 to 80% for a single crystal, and from 72 to 85% for a pellet according to the polish.

It is remarkable that a pellet should sometimes reflect as much as a single crystal if the surface is good:
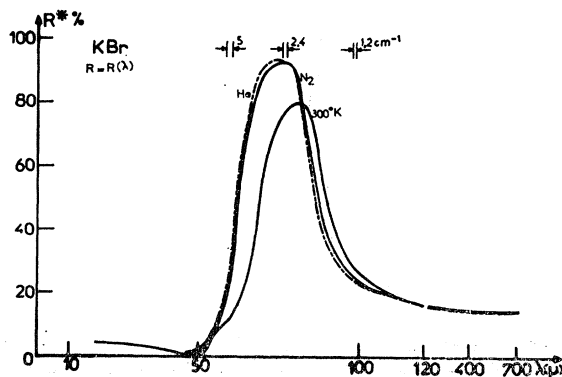
FIG. 2. Reflectivity of KBr at three temperatures for a 15° angle of incidence. Note the position λ_M of the reflection maximum: $\lambda_M(300°K) = 81\mu$; λ_M(liquid nitrogen) $= 75.5$ μ; λ_M(liquid helium) $= 74.5$ μ.
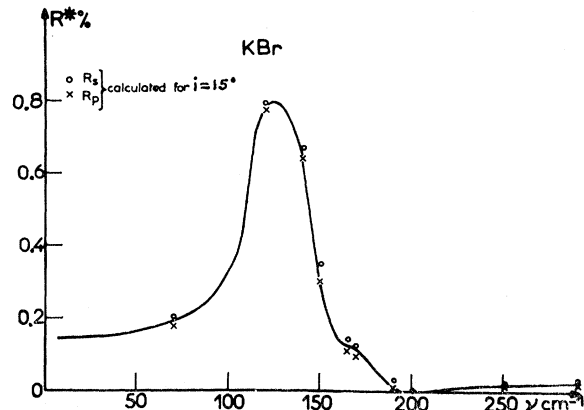
FIG. 3. At an incident angle of 15°, Fresnel's formulas show that R_s never exceeds R_p by more than a few percent. The curve calculated for normal reflection (solid line) passes between the R_s and R_p curves for the incidence angle of 15°.

We have already noticed this fact in the case of the copper halides,[11] and of the sintered materials sold by Kodak under the name of "Irtran,"[6] but it was no longer true for ZnTe, for example,[6] for which the peak reflectivity of the pellet prepared in the laboratory was rather weaker than for the Irtran one. The damping δ of the oscillators responsible for the reflectivity thus depends mainly on the quality of the surface. From a macroscopic point of view, the reflectivity is mainly affected at the peak in the reflectivity, because the index of absorption k is high, so the skin depth $\rho = \lambda/4\pi k$ is small.

Here, $\lambda \cong 80$ μ and $k \cong 5$; hence $\rho \cong 1.2$ μ. It might be possible for the surface to be chemically or physically disturbed to that depth. For example, tensions, varying according to the point considered, could modify the lattice dynamics and in particular the resonance frequency. Forbidden modes could also become active.[12] However, the most troublesome physical disturbance in our case is simply the roughness of the surface, since we have seen that a well-polished KBr pellet reflects as well as a single crystal.

It has been shown[13] that the influence of the wrinkles on the thermal radiation of a surface can be very important, even if the defects have dimensions smaller than the wavelengths considered. The calculation is
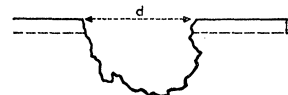
FIG. 4. When the average size d of the holes in the reflecting surface is much greater than the skin depth ρ, the reflectivity varies like the difference between the total area S, and the area s of the holes.

[11] J. N. Plendl, A. Hadni, J. Claudel, Y. Henninger, G. Morlot, P. Strimer, and L. C. Mansur, Appl. Opt. **3**, 397 (1966).
[12] A. S. Barker, Jr., Phys. Rev. **132**, 1474 (1963).
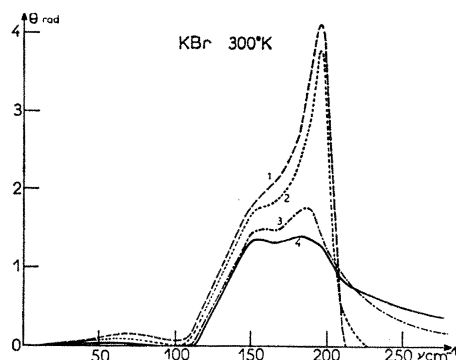[13] B. Py, thesis, Université de Nancy, 1967 (unpublished).

FIG. 5. Phase shift θ in the reflection as a function of ω for four values of R_{min}*: R_{min}*=0.00001 (curve No. 1); R_{min}*=0.0001 (curve No. 2); R_{min}*=0.01 (curve No. 3); R_{min}*=0.02 (curve No. 4).
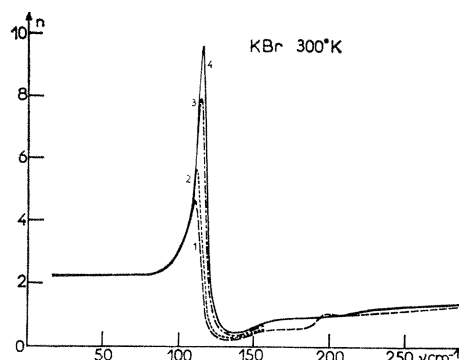

FIG. 6. Refractive index n of KBr at room temperature for four values of R_{min}*: R_{min}*=0.00001 (curve No. 1); R_{min}*=0.0001 (curve No. 2); R_{min}*=0.01 (curve No. 3); R_{min}*=0.02 (curve No. 4).

simple when the skin depth ρ of the crystal is much smaller than the size of the holes (Fig. 4). In this case, the reflectivity of the polished surface must be multiplied by a factor $K<1$, $K=(S-s)/S$, where S is the whole surface and s is the surface of the pores. Effectively in the s surface, there is a lack of the electrons needed for a specular reflection. The effect will occur only in the part of the spectrum where $\rho<d$, that is, where k is high.

B. Analysis of Normal Reflectivity Spectra

1. Havelock's Formula

In 1924, Havelock[14] gave an approximative formula linking the wavelength λ_M of the maximum of reflectivity to the wavelength λ_0 of the resonance, using the values ϵ_{R0} and ϵ_{RV} of the static and the high-frequency dielectric constant:

$$\frac{\lambda_0}{\lambda_M} = 1 + \frac{\epsilon_{R0} - \epsilon_{RV}}{\epsilon_{RV} - 4}. \qquad (5)$$

Because of a lack of data at low temperature, we shall

TABLE I. Characteristic phonon frequencies from neutron diffraction at 90°K.[a]

Phonon	Frequency (10^{-12} cps)	Wave number (cm^{-1})
TO [000]	3.60±0.03	120±1
LO [000]	5.00±0.05	162±1.6
LA [001]	2.15±0.03	72±0.8
TA [001]	1.25±0.02	42±1
LO [001]	4.02±0.07	134±0.02
TO [001]	3.72±0.04	124±1
LA [½½½]	2.82±0.04	94±1
TA [½½½]	2.20±0.03	74±1
LO [½½½]	4.34±0.05	145±1.3
TO [½½½]	3.06±0.05	102±1.3

[a] See Ref. 9.

[14] T. M. Havelock, Proc. Roy. Soc. (London) **A105**, 488 (1924).

take $\epsilon_{RV}=2.45=$const. On the other hand, we have recent data for ϵ_{R0} which we have collected in Table II, together with the values of λ_0 calculated from λ_M with Havelock's formula. We have also given values of λ_0 obtained either by other spectroscopic methods or by neutron diffraction; the agreement is good, especially at low temperatures.

2. Kramers-Kronig Analysis

The Kramers-Kronig analysis is, for instance, the method used by Karo et al., to analyze the reflectivity spectrum of NaCl, KCl, LiF, and NaF at 300 and 100°K. They only retain $n(\omega)$ and calculate $k(\omega)$ from the transmission spectra.

We first have to compute the phase shift θ at the reflectivity[15] by the relation

$$\theta(\omega_0) = \frac{1}{\pi} \int_0^\infty \frac{dA}{d\omega} \ln \left| \frac{\omega+\omega_0}{\omega-\omega_0} \right| d\omega, \qquad (6)$$
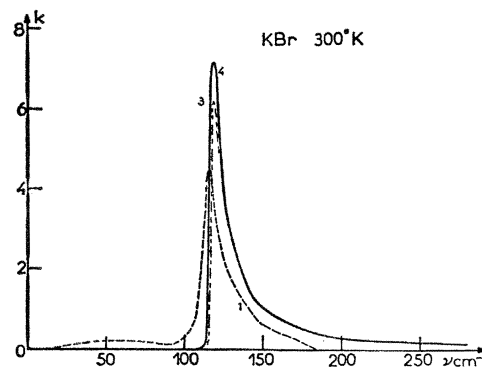
with $A=\ln[(1/R)^{1/2}]$. We see in Fig. 2 that the re-

FIG. 7. Absorption index k of KBr at room temperature for three values of R_{min}*: R_{min}*=0.00001 (curve No. 1); R_{min}*=0.01 (curve No. 3); R_{min}*=0.02 (curve No. 4). From now on we shall only retain curve No. 3.

[15] T. S. Robinson and W. C. Price, in *Molecular Spectroscopy* edited by G. Sell (Oxford University Press, London, 1955), p. 211.
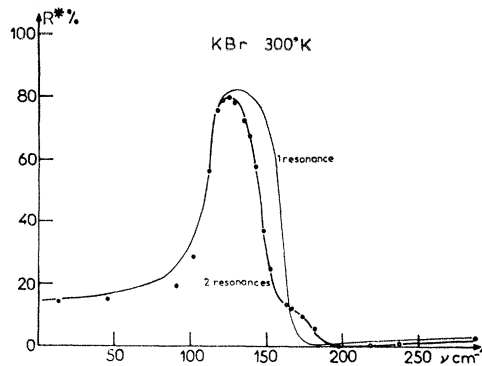
FIG. 8. Lorentz analysis of KBr reflectivity at room temperature with one oscillator (thin line): $\nu_1=113.9$ cm^{-1}; $\rho_1=0.198$; $\delta_1=0.052$; and with an additional weaker oscillator (thick line): $\nu_2=165$ cm^{-1}; $\rho_2=0.015$; $\delta_2=0.23$. The points give the observed reflectivity.

FIG. 10. Lorentz analysis of KBr reflectivity at liquid-helium temperature with one oscillator (thin line): $\nu_1=121$ cm^{-1}; $\rho_1=0.17$; $\delta_1=0.016$; and with an additional weaker oscillator (thick line): $\nu_2=178$ cm^{-1}; $\rho_2=0.004$; $\delta_2=0.23$.

flectivity R shows a minimum value at about 50 μ which can only be specified as being between 2×10^{-2} and 0.5×10^{-2}, so the term in $1/R$ can only be located between the limit values 50 and 200, and we see that this lack of accuracy on one point of the reflectivity spectrum (where R is a minimum) will affect the whole spectrum of θ, n, or k. Figure 5, for example, gives four curves of $\theta(\omega)$ for $R_{\min}$, respectively, equal to 10^{-5}, 10^{-4}, 10^{-2}, and 2×10^{-2}. The first two seem unacceptable, for they give a maximum of θ greater than π rad. Applying the relations

$$n=\frac{1-|r|^2}{1-2|r|\cos\theta+|r|^2}, \qquad (7)$$

$$k=\frac{-2|r|\sin\theta}{1-2|r|\cos\theta+|r|^2}, \qquad (8)$$

we get four curves giving the refractive index n (Fig. 6), and four curves giving the index of absorption k (Fig. 7). We notice that for $R_{\min}=10^{-5}$ and 10^{-4}, the quantity
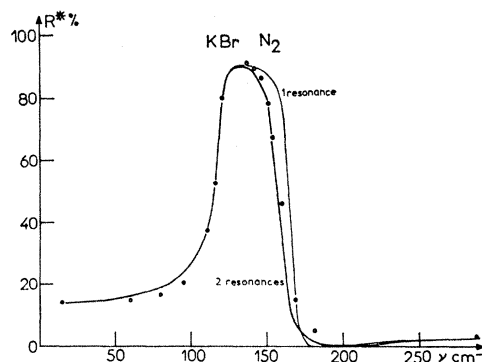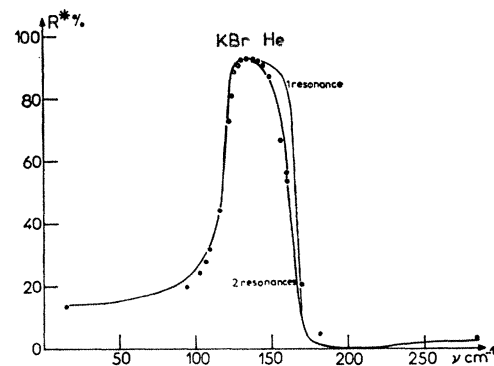

FIG. 9. Lorentz analysis of KBr reflectivity at liquid-nitrogen temperature with one oscillator (thin line): $\nu_1=119.2$ cm^{-1}; $\rho_1=0.176$; $\delta_1=0.022$; and with an additional weaker oscillator (thick line): $\nu_2=175$ cm^{-1}; $\rho_2=0.005$; $\delta_2=0.23$. The points give the observed reflectivity.

θ exceeds the value π twice resulting in two maxima for n (Fig. 8). These two $R_{\min}$ values being eliminated, we see in Fig. 8 that curves 3 and 4, which give the refractive index corresponding to $R_{\min}$ equal to 10^{-2} and 2×10^{-2}, respectively, are very similar in the whole spectrum, except perhaps in the vicinity of the resonance frequency. The same is true for k. The method is thus valid, except in the immediate vicinity of the resonance, where we must make the curves n and k more precise with the help of supplementary data, which are given, for example, by the transmission spectrum.

In Fig. 8 and 9, respectively, corresponding to n and k at 300°K, we shall retain curve 3 ($R_{\min}=0.01$). For lower temperatures, we refer to a preceding paper.[6]

3. Lorentz Analysis

Because of their complexity, the reflectivity spectra of the alkali halides are generally not analyzed in terms of harmonic oscillators.[16] In the case of KBr, where the reflectivity spectra are the simplest, we have, however, tried, using successively one and two resonances.

Since ϵ_{R0} is known at every temperature with a good accuracy, $\rho_1=(\epsilon_{R0}-\epsilon_{RV})/4\pi$ is precisely determined for one resonance analysis. In addition the transmission spectra give an approximate value of ν_1. The damping

TABLE II. Dielectric constant, wavelength of maximum reflectivity, and TO wavelength versus temperature.

	Liquid-helium temperature	Liquid-nitrogen temperature	Room temperature
ϵ_{R0} (Lowndes)	4.52 ± 0.02 (1.5°K)	4.64 ± 0.02	4.90 ± 0.02
$\lambda_M(\mu)$ (observed)	$74.5\ \pm2.5$	$75.5\ \pm2.5$	$81\ \pm3.5$
$\lambda_0(\mu)$ (Havelock)	84	84.7	92
(transmission)	83	84.2	88.3
(Kramers-Kronig)	81.5	82.5	87
(Cowley)		$83.5\ \pm0.7$	

[16] E. Burnstein, in *Phonons and Photons Interactions*, edited by T. A. Back (W. A. Benjamin, Inc., New York, 1964).
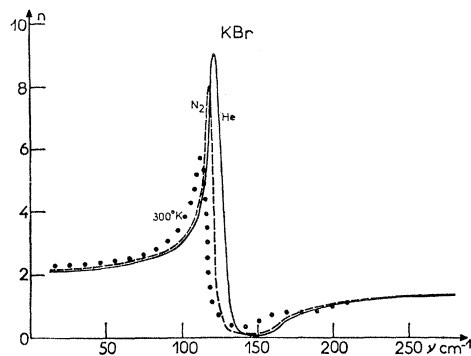
FIG. 11. KBr refractive index n from a two-linear-oscillator analysis.

TABLE III. Frequency of maximum absorption, and Lorentz parameters, at four different temperatures.

Temperature (°K)	ϵ_{RV}[a]	ϵ_{R0}[b]	ν_1 (cm^{-1})	$\nu_M(k$ max) (cm^{-1})	ν_2[c] (cm^{-1})	ρ_1	ρ_2	δ_1	δ_2
800	...	...	95[d]	...	...	...	...	...	...
300	2.40	4.85	113.9	115.5	165	0.198	0.015	0.052	0.23
80	2.43	4.66	119.2	120	175	0.176	0.005	0.022	0.23
18	2.46	4.59	121	121.5	178	0.17	0.004	0.016	0.23

[a] We have taken $n_V = 1.55$ at 290°K, and $(\partial n/\partial T)_P = -0.4 \times 10^{-4}$ (°K)$^{-1}$ [A. J. Bosman and E. E. Havinga, Phys. Rev. **129**, 1593 (1963)].
[b] We have tried to give to ϵ_{R0} values compatible with Lowndes's recent measurements [R. P. Lowndes, Phys. Letters **100**, 752 (1955)].
[c] The reflectivity curve no longer showing a precise secondary maximum when the temperature is lowered, the values given for ν_2 at 80 and 18°K are probably very inaccurate.
[d] From J. E. Mooij, Phys. Letters **24**, A249 (1967).

parameter δ_1 is still to be determined to find a reflectivity curve close to the experimental one. By a least-squares method, we then modify ν_1 and δ_1 very slightly to represent exactly the low-frequency part of the reflectivity curve, where the second resonance $\nu_2 > \nu_1$ has no appreciable effect. Figures 8, 9, and 10 give the best results obtained at the three temperatures considered. The curve fits the low-frequency wing, but on the other wing it first gives too high a reflectivity, and then cuts the experimental curve, and gives a reflectivity slightly too weak.

At room temperature, ν_2 is approximately given by the point of inflexion of the reflectivity: ρ_2 and δ_2 are obtained by successive approximation. The secondary maximum of reflectivity thus appears, the minimum moves towards higher frequencies, the width of the reflectivity band decreases, and the computed reflectivity fits the experimental measurements (Fig. 10). We can thus accept the eight parameters characterizing two Lorentz oscillators as capable of representing the reflectivity of potassium bromide in the whole infrared (Table III).

Then, we can compute the dispersion curve for the refractive index n (Fig. 11) and for the index of absorption k (Fig. 12) at the three temperatures, with the
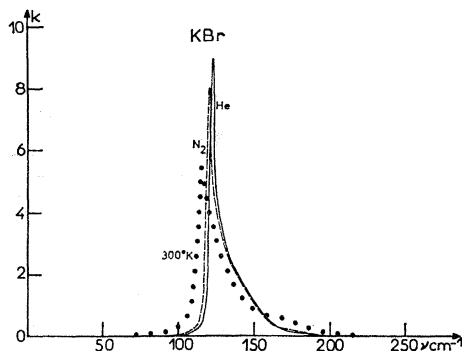
classical formulas

$$\epsilon' = n^2 - k^2 = \epsilon_{RV} + \sum_{j=1}^{n} 4\pi\rho_j \frac{1-\Omega_j^2}{(1-\Omega_j^2)^2 + \delta_j^2\Omega_j^2}, \quad (9)$$

$$\epsilon'' = 2nk = \sum_{j=1}^{n} 4\pi\rho_j \frac{\delta_j\Omega_j}{(1-\Omega_j^2)\delta_j^2\Omega_j^2}, \quad (10)$$

with $\sum_j 4\pi\rho_j = \epsilon_{R0} - \epsilon_{RV}$. δ_j represents the reduced damping factor and $\Omega_j = \nu/\nu_j$ the reduced frequency. We remark that ν_M is somewhat higher than ν_1 for high temperatures. This is probably due to the second resonance, the strength of which increases with temperature.

III. REFLECTIVITY SPECTRA UNDER HIGH INCIDENCE

All alkali halides show a secondary maximum of reflectivity[8,17,18] generally associated with addition processes. For KBr, this maximum is the less visible one
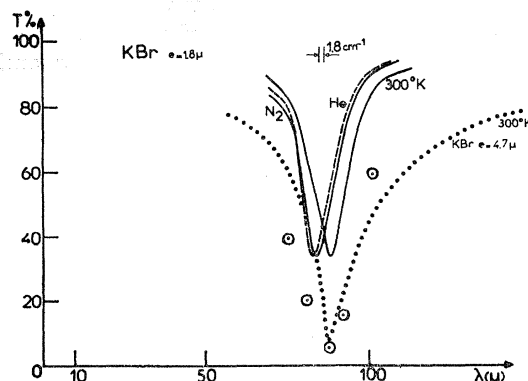

FIG. 13. Transmission of two KBr layers deposited by evaporation, one on Mylar film, thickness 4 μ (dotted line), the other on quartz plate, thickness 2 mm (full and dashed line). The circled dots give the true transmission $T^* = e^{-Kd}$ calculated from Fig. 14.

FIG. 12. KBr absorption index k supposing two linear oscillators.

[17] A. Mitsuishi, H. Yoshinaga, and S. Fujita J. Phys. Soc. Japan **14**, 110 (1959).
[18] M. Czerny, Z. Physik, **65**, 600 (1930).

TABLE IV. Calculation of compressibility and effective charge at three different temperatures from Szigeti's relations.

Tempera-tures (°K)	a (cm)	n_V	ϵ_{R0} (Lorentz)	(cm²/dyne) χ_T	χ/χ_0	e^*(cgs esu)	e^*/e
290	6.599×10^{-8}	1.55	4.85	6.36×10^{-12}	0.982	3.59×10^{-10}	0.75
80	6.566×10^{-8}	1.56	4.66	5.95×10^{-12}		3.56×10^{-10}	0.74
18	6.558×10^{-8}	1.57	4.59	5.87×10^{-12}		3.53×10^{-10}	0.74

at 160 cm^{-1} (Fig. 2), and it even disappears at low temperatures. From Yoshinaga, we know that its intensity increases with the angle of incidence, but he did not analyze this enhancement. This maximum leads to a small peak in the absorption spectrum (Fig. 12) at 165 cm^{-1} for room temperature, which might correspond to TO$[\frac{111}{222}]$+TA$[\frac{111}{222}]$=176 cm^{-1} $\simeq$LO$[000]$=162 cm^{-1} from Cowley's measurements at 90°K (Table I), and Burstein's selection rules for two-phonon combinations.

IV. TRANSMISSION SPECTRA OF VERY THIN PLATES

Figure 13 gives the transmission under quasinormal incidence of thin KBr layers, prepared by evaporation on Mylar film, or on quartz plates in vacuum. Let us denote by d the thickness of the layer, by d' that of the support, and by n and n' their refractive indexes, and let us write $M=2\pi d/\lambda$ and $M'=2\pi d'/\lambda$. Since both M and M' are small compared to unity in the case of the Mylar film, we can use the formulas cited by Abeles and Mathieu,[19] which give the apparent transmission T:

$$T=\frac{4}{(2+2nkM)^2+[(n^2-k^2-1)M+(n'^2-1)M']^2}. \quad (11)$$

After writing $A=(1+R)/(1-R)$, the authors show that n is given by

$$[(1-A^2)^2M^2+4]M^2n^4-8AM^2n^3$$
$$+2[2+(1-A^2)(1/T-1)]M^2n^2+(1/T-1)^2=0. \quad (12)$$

Knowing n from this relation, we get k from

$$k^2=2An-(n^2+1).$$

These k values plotted in Fig. 14 are in good agreement with the k values determined from the Lorentz analysis (dark circles), except perhaps in the immediate vicinity of the resonance. In Fig. 13, we also notice in the case of the Mylar film that on the short-wavelength side of the band, the true transmission $T^*=e^{-Kd}$ is smaller than the measured transmission T, as at first might be surprising. In fact, this discrepancy is probably the result of constructive interference for this wavelength range. We also remark that there is no significant change of the minimum value of the apparent transmission T when the quartz plate with the KBr layer is cooled, which is slightly in contradiction with Fig. 12.

Figure 15 gives the transmission spectrum of a thin KBr layer deposited on a brass plate and receiving an infrared beam under a high angle of incidence. We know from Berreman's experiments on LiF, for instance, that under these conditions, a minimum of transmission is seen for ν_L and a sharper one for ν_T.[20] Our results (Fig. 15) are in good agreement with these measurements, therefore we take $\lambda_L\simeq61$ μ and $\lambda_T\simeq90$ μ.
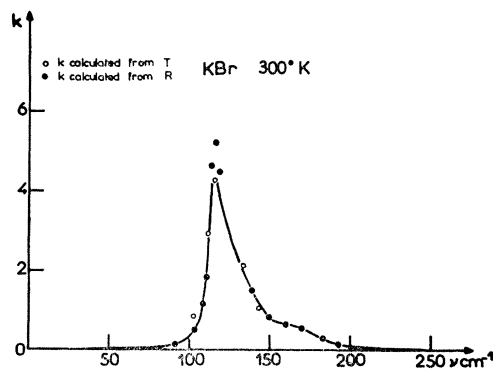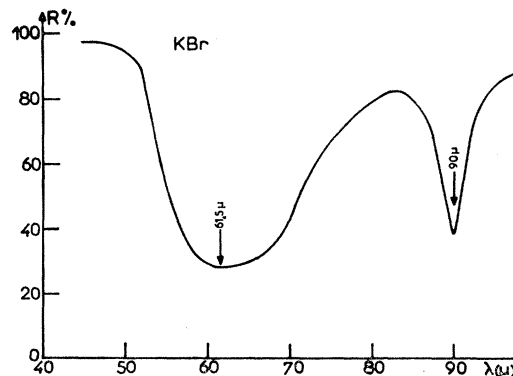

FIG. 14. Transmission measurements allow us to make more precise the values obtained by Lorentz analysis for the absorption index k.

FIG. 15. Reflectivity of a brass plate covered with a thin KBr layer, for a 60° angle of incidence and polarized radiation (p component).

[19] F. Abeles and J. P. Mathieu, Ann. Phys. (Paris) **3**, 5 (1958).
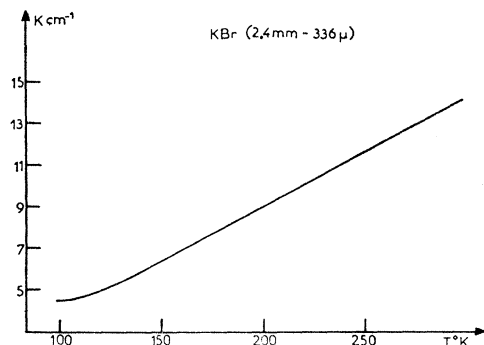
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FIG. 16. For 337 μ wavelength, the absorption coefficient K of KBr is proportional to the absolute temperature between 80 and 300°K.

V. APPLICATION OF SZIGETI'S FORMULAS TO KBr

From Szigeti's first formulas,[21] the coefficient of compressibility X can be calculated from ν_T:

$$X = 3\frac{n^2+2}{\epsilon+2}\frac{a^3}{4R^2\beta};\tag{13}$$

$a^3/4$ is the volume occupied by a molecule, and $\beta = 4\pi^2\mu\nu_T^2$, with $1/\mu = 1/M + 1/m$. The edge a of the cubic unit cell measures 6.599×10^{-8} cm at 300°K,[22]and the distance R between the halogen and the four nearest potassium atoms is equal to $a/2$. We know the value of a at room temperature and liquid-helium temperature, but we had to extrapolate for 18 and 80°K. The calculations are summed up in Table IV, where X_0 represents the measured value of the compressibility coefficient, which is known only at room temperature. The agreement between theory and experiment is good at room temperature. At low temperature, we see that X_T de-
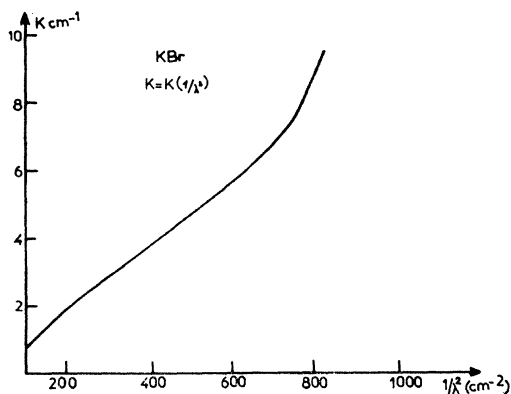

FIG. 17. For very long wavelengths between 1000 and 375 μ, the absorption coefficient K is approximately proportional to $1/\lambda^2$.

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[22] *Structure Reports*, edited by N. V. A. Oosthoek and M. I. J. Uitgevers (International Union of Crystallography, Utrecht, Netherlands, 1947), Vol. 11, p. 485.
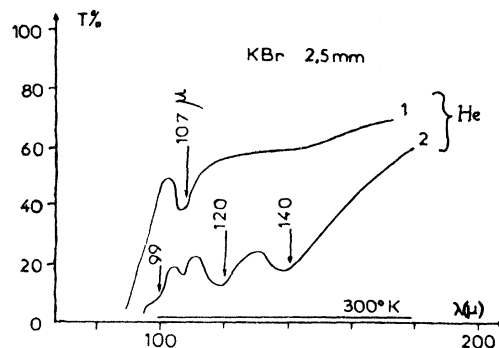
FIG. 18. The transmission of a thick KBr plate (e=2.5 mm) is zero at room temperature. At liquid-helium temperature, KBr becomes transparent when pure (curve No. 1) except at 107 μ. The addition of Na$^+$ ions (curve No. 2) results in the appearance of three bands at 99, 120, and 140 μ. We can also increase the intensity of the 107 μ band by the addition of chlorine ions.

creases without approaching zero, which is as expected; but we do not have any measured value of X_0 to check the theory.

Szigeti's second formula,

$$(e^*)^2 = \frac{9}{16\pi}\beta a^3\frac{\epsilon_{R0}-n^2}{(n^2+2)^2},\tag{14}$$

allows the calculation of e^*/e. We see in Table IV that the ratio is nearly constant and much smaller than 1 in spite of the wholly ionic character of the link.

VI. TRANSMISSION OF THICK PLATES IN THE VERY FAR INFRARED

A. Pure Crystals

Over the last few years,[5,6] we have shown that all crystals become completely transparent in the far infrared when they are sufficiently cooled,[23] while the transmission of glasses is not modified.[24] This super-transparency has been explained in terms of phonon-difference processes.[25] Between 300 and 80°K, we see in Fig. 16 that K varies like T, at least for $\lambda = 336$ μ. The measurements are made with the laboratory CN laser, which allows an accuracy better than 1% on transmission measurements.[26] As regards the wavelength dependence, the absorption coefficient at room temperature is approximately proportional to $1/\lambda^2$ from 1000 to 350 μ (Fig. 17).

B. Induced Absorption by Impurities

The residual absorption of potassium bromide at low temperature gives only one peak at 93 cm^{-1} for the

[23] A. Hadni, J. Claudel, X. Gerbaux, G. Morlot, and J. M. Munier, Appl. Opt. **4**, 487 (1965).

[24] A. Hadni, G. Morlot, X. Gerbaux, D. Chanal, F. Brehat, and P. Strimer, Compt. Rend. **260**, 4973 (1965).

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[26] A. Hadni, R. Thomas, and J. Weber, J. Chim. Phys. **64**, 71 (1967).

purest crystals we could make (Fig. 18). The addition of Na$^+$ ions results in the appearance of three new bands at 101, 83.5, and 71.5 cm^{-1} (Fig. 18), of the same frequencies as the three maxima in the lattice-mode density,[9] and corresponding approximately to characteristic TO, LA, and TA phonons. Except for Na$^+$, all impurities give only a general background absorption. The same is true for neutron irradiation, except in the narrow phonon gap of KBr around 93 cm^{-1}, where the absorption does not increase.[27] Chlorine seems to induce a localized vibration at the limit of the gap: this should explain the residual peak at 93 cm^{-1} we found in the purest crystal, which still contained a small amount of chlorine.

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[27] A. Hadni, G. Morlot, and F. Brehat, Compt. Rend. **264**, 164 (1967).

VII. CONCLUSIONS

The optical constants of potassium bromide (ν_T, δ_1, ρ_1, k_M, ϵ_{R0}, and χ_T) vary linearly with temperature within the experimental accuracy. Lorentz theory permits us to consider two linear oscillators, which represent quite well the behavior of KBr, if they are modified to include a temperature dependence. The damping of the fundamental oscillator decreases when T decreases. On the other hand, its strength does not vary much, while the strength of the second oscillator decreases strongly.

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Scattering of Phonons by Monatomic Impurities in Potassium Halides*

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The thermal conductivity of doped KCl, KBr, and KI has been measured between 1 and 200°K. Below ~5°K, the phonon scattering by the defects obeys a Rayleigh law in most cases. The magnitude of the scattering is determined by the mass difference alone. In Ag$^+$-doped crystals, however, the Rayleigh scattering is much weaker than predicted by the mass difference. This is explained through the weak coupling between the Ag$^+$ and its neighbors. Above 5°K, in the region of the resonance scattering, the conductivity can be qualitatively described with the model of elastic phonon resonant scattering by quasi-localized modes. In KCl:Tl, I, Rb, and Br, the mass difference alone suffices to qualitatively describe the data, which means that the resonant mode is odd. The resonant scattering observed in Li$^+$- and Ag$^+$-doped crystals is ascribed to excitations of even resonant modes. It is noted that in many cases thermal-conductivity measurements are complementary to optical-absorption measurements, since the former observe defects strongly coupled to the lattice, whereas the latter observe the ones which are weakly coupled.

I. INTRODUCTION

THE increasing recognition of the importance of lattice vibrations for many solid-state phenomena has stimulated numerous theoretical and experimental studies of lattice vibrations in defect crystals.[1] Defects change the vibrational spectrum of the lattice by causing new modes which can not be described as plane waves, but which are centered around the defect and whose amplitude decreases with increasing distance

from the defect. Such impurity modes can have frequencies which lie in the frequency spectrum of the unperturbed lattice. If they are strongly coupled to the plane-wave phonons, they will impede the heat flow in the crystal and can thus be detected through measurements of the lattice thermal conductivity.[2-6] By investigating a large number of foreign alkali or halogen ions dissolved in the host lattices KCl, KBr, and KI, and by comparing the results with those obtained by far

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[2] C. T. Walker and R. O. Pohl, Phys. Rev. **131**, 1433 (1963); interpretation by M. C. Wagner, *ibid.* **131**, 1443 (1963).

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