mainly due to nonparabolicity rather than to Kaw's model. Superficially it could appear that results of Kaw may have insignificant contributions to nonlinearity since the conclusions are derived as a second-order effect to the electronic motion. Recent extension of Kaw's model by KP, however, shows that nonlinear mixing is a first-order effect if the laser frequency is very much greater than τ_0. If $\omega\tau_0$ is exceedingly large, as can be seen from Eq. (17), then the relative importance of nonlinearity due to BWL is greater than that due to the relaxational process. At low temperatures (~ 4 °K) and with samples with large impurity concentration, it may be concluded that the relaxational contribution to nonlinearity may exceed the contribution from nonparabolicity.

ACKNOWLEDGMENT

The authors wish to thank Dr. M. Kriechbaum for his help in the computation.

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*Research partly supported by the National Research Council of Canada.

[1] C. K. N. Patel, R. E. Slusher, and P. A. Fleury, Phys. Rev. Letters 17, 1011 (1966).

[2] P. A. Wolf and G. A. Pearson, Phys. Rev. Letters 17, 1015 (1966).

[3] P. Kaw, Phys, Rev. Letters 21, 539 (1968).

[4] B. S. Krishnamurthy and V. V. Paranjape, Phys. Rev. 181, 1153 (1969).

[5] R. W. Bierig, M. H. Weiler, and B. Lax, Phys. Rev. 186, 747 (1969).

[6] B. Lax, W. Zawadzki, and M. H. Weiler, Phys. Rev. Letters 18, 462 (1967).

[7] In the earlier work (KP), there was, unfortunately, numerical error in the expression for A.

[8] J. J. Wynne, Phys. Rev. 178, 1295 (1969).

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Longitudinal-Optical Phonons in TiO$_2$ (Rutile) Thin-Film Spectra

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(Received 4 September 1970)

The infrared spectra of oxidation films on titanium show an asymmetrical absorption band at 828 cm^{-1} not found as an infrared-active mode in single-crystal TiO$_2$. It is identified as two superposed longitudinal-optical modes at approximately 828 and 809 cm^{-1} on the basis of optical tests and theoretical predictions.

In the course of investigating the infrared reflection spectra of polycrystalline oxidation films on titanium and titanium-based alloys,[1] one absorption band is found at 828 cm^{-1} which is not identifiable with infrared-active modes of rutile reported in the literature. Figure 1 shows typical reflection spectra of two such films in p-polarized radiation at 15° angle of incidence, obtained on a PE No. 225 grating spectrophotometer with a wire grid polarizer. The starting material was RMI 30 titanium sheet electropolished to a mirror finish and then oxidized in the temperature range 500–825 °C in a 0.2 O$_2$/0.8 Ar atmosphere for various periods of time up to 16 h. The $\frac{1}{2}$-h spectrum is typical of those of the thinner films, showing channel spectra in the region of transparency and absorption bands below 1000 cm^{-1}. The 2-h spectrum approaches that of the single-crystal rutile where the reststrahlen structure is prominent including the reflection minima around 870 cm^{-1}. Only rutile is detected in these films by x-ray diffraction.

The bands at 470 and 370 cm^{-1} are clearly identified with two of the ordinary-ray E_u modes reported by Spitzer *et al.*[2] in the single crystal. Another single-crystal study by Liebisch and Rubens,[3] however, is in error. They find no band around 370 cm^{-1} in the ordinary ray but instead one at 408 cm^{-1} in the extraordinary ray. (Spitzer's results were confirmed with a natural rutile crystal in this laboratory.) Both references report weak broad reflection minima around 670 and 570 cm^{-1} which are also observed in many of these thin-film spectra. Neither indicates any bands present around 828 cm^{-1}.

The 828-cm^{-1} band is believed to be two superposed longitudinal-optical (LO) modes of rutile for the following reasons:

(1) The band appears only in the thinner films and is not present in the thicker films in which the reststrahlen structure becomes prominent.

(2) It is present only in p-polarized radiation.

(3) It is more intense at 32° than at 15° angle of incidence. These properties, cited by Berreman[4] as characteristics of LO-mode absorption bands, are illustrated in Fig. 2.

With the aid of an analog curve resolver, it is possible to find two Gaussian components in this

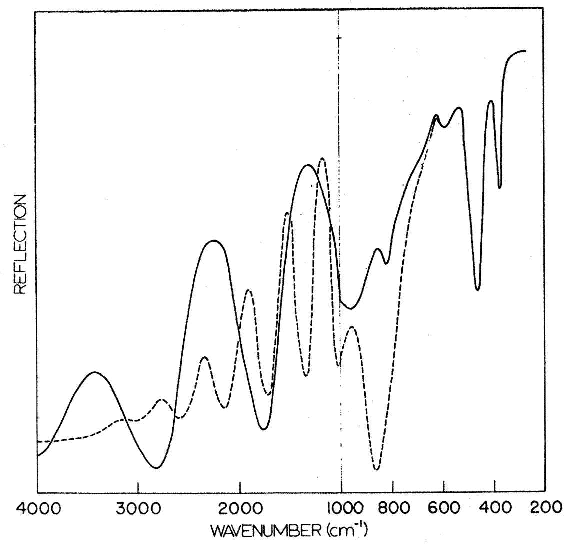

FIG. 1. Reflection spectrum of titanium oxidized at 700 °C. Solid curve: $\frac{1}{2}$ h. Broken curve: 2 h, p-polarized radiation.

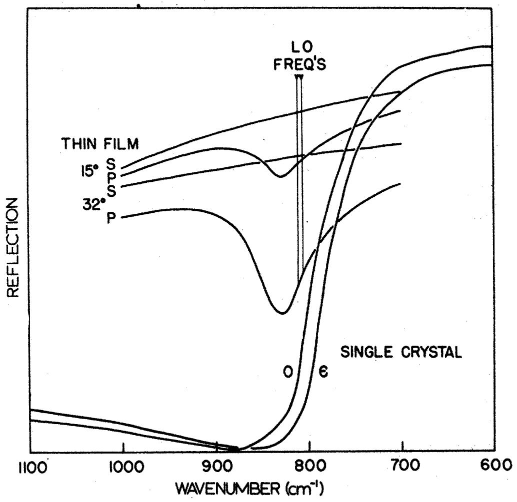

FIG. 2. Reflection spectra of single-crystal rutile (redrawn from Ref. 2) and oxidized titanium films at two angles of incidence and in p- and s-polarized radiation. LO-mode frequencies from Ref. 5 are indicated.

band at 828 and 809 cm^{-1}, with half-widths of about 60 and 120 cm^{-1}, respectively. Eagles[5] reports two LO-mode frequencies in rutile at 811 cm^{-1} in the extraordinary ray and 806 cm^{-1} in the ordinary ray, calculated from single-crystal measurements. The small discrepancy is possibly due to accumulated errors in the experimental data used in the calculations.

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[1] S. R. Lyon and C. M. Phillippi (unpublished).

[2] W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. 126, 1710 (1962).

[3] Th. Liebisch and H. Rubens, Sitzber. Preuss. Akad. Wiss., Physik-Math Kl. 8, 211 (1921).

[4] D. W. Berreman, Phys. Rev. 130, 2193 (1963).

[5] D. M. Eagles, J. Phys. Chem. Solids 25, 1243 (1964).

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Pseudopotential Calculations of Spin Susceptibility and Grüneisen Parameters for Alkali Metals

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A modified form of Harrison's model pseudopotential has been used to calculate the spin susceptibility and the Grüneisen parameters of alkali metals: viz., lithium, sodium, and potassium. These results are in good agreement with the available experimental data.

I. INTRODUCTION

The pseudopotential formalism for representing the electron-ion interaction in simple metals has been extensively employed by a number of workers.[1–4] Recently, the present authors employed a local-pseudopotential model to calculate the lattice-dynamical properties (e.g., phonon dispersion rela-

TABLE I. Parameters of the model pseudopotential.

Element	Effective mass (m^*/m)	β (Ry a.u.^{3})	$\rho=\gamma_c$ (a.u.)
Lithium	1.45	18.3	0.2
Sodium	0.98	32.7	0.3
Potassium	0.93	59.23	0.4