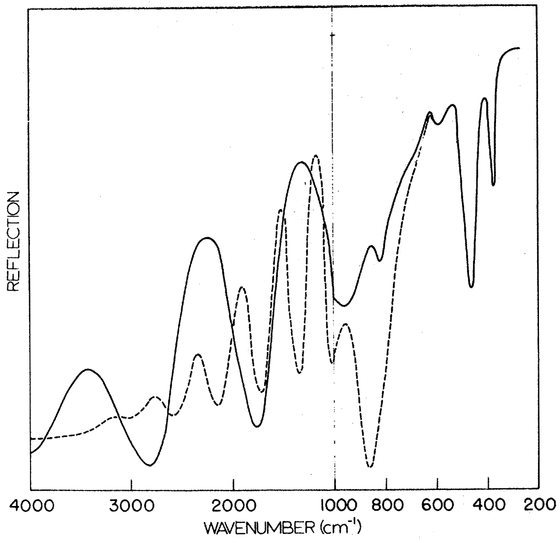

FIG. 1. Reflection spectrum of titanium oxidized at 700 °C. Solid curve: $\frac{1}{2}$ h. Broken curve: 2 h, $p$-polarized radiation.

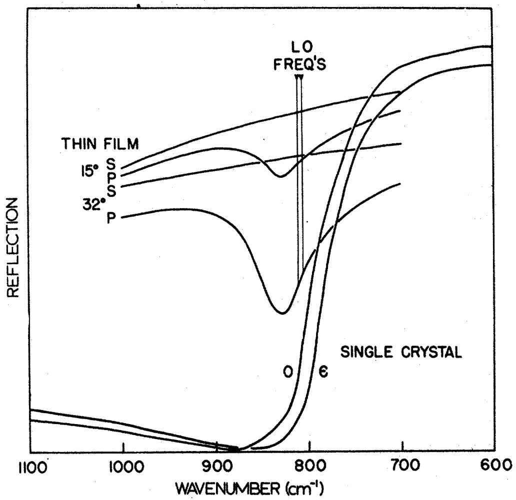

FIG. 2. Reflection spectra of single-crystal rutile (redrawn from Ref. 2) and oxidized titanium films at two angles of incidence and in $p$- and $s$-polarized radiation. LO-mode frequencies from Ref. 5 are indicated.

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[1] S. R. Lyon and C. M. Phillippi (unpublished).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 ($m^*/m$) | $\beta$ (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 |

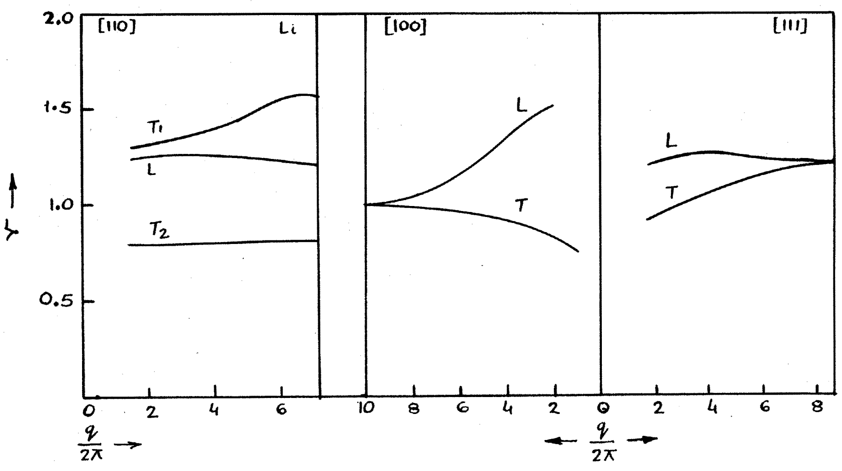

FIG. 1. Calculated Grüneisen parameters for lithium in [100], [110], and [111] directions; $q/2\pi$ is in units of $1/10a$.

tions, binding energy, compressibility, etc.) of aluminum,[5] sodium,[6] potassium,[7] and lithium.[8] A calculation of the electrical properties of the liquid metals was also reported[9] based on the pseudopotential approach. The same model is adopted here to calculate the spin susceptibility and the Grüneisen parameters of bcc lithium, sodium, and potassium. The calculations are presented in Sec. II and the results are discussed in Sec. III.

## II. DESCRIPTION OF CALCULATIONS

Saxena and Bhattacharya[10] have recently reported their theoretical results on the spin susceptibility of sodium taking into account the electron-phonon and the electron-lattice interactions. The effect of the Fermi, exchange, and correlation energies on the spin paramagnetism of the alkali metals has been included on the lines of Abe.[11] The effect of the electron-phonon interaction on the spin paramagnetism is of the order of $\sqrt{(m/M)}$ as shown by Migdal[12] and by Quinn and Ferrell,[13] where $m$ and $M$ are the masses of electron and ion, respectively. It has been, neglected therefore, in the present calculations. The expression for the crystal-lattice contribution to the spin susceptibility is the same as given by Saxena and Bhattacharya[10]:

$$A_L = -\frac{2\gamma_s^2}{9(12\pi^2)^{1/3}} \times \sum_{q\neq 0} \frac{|\omega_b(q)|^2}{x^2-1}\left[1+\frac{1-x^2}{2x}\ln\left|\frac{1+x}{1-x}\right|\right]. \tag{1}$$

Here $\gamma_s$ is the radius of the sphere whose volume is the average conduction-electron volume; $x = q/2k_F$, $k_F$ being the Fermi wave vector; and $\omega_b(q)$ is the bare pseudopotential, given by

$$\omega_b(q) = \frac{1}{\Omega_0}\left[-\frac{4\pi z e^2}{q^2} + \frac{\beta e^{-\rho q}}{(1+q^2\gamma_c^2)^2}\right]. \tag{2}$$

An exponential term has been introduced in the repulsive part of the Harrison model pseudopotential.[14] The introduction of an exponential term simplifies the computations significantly because of the rapid convergence of the electronic term.

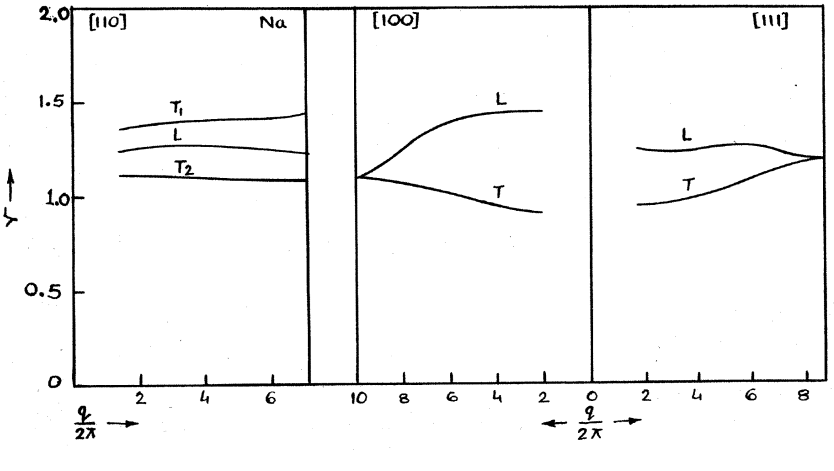

FIG. 2. Calculated Grüneisen parameters for sodium in [100], [110], and [111] directions; $q/2\pi$ is in units of $1/10a$.

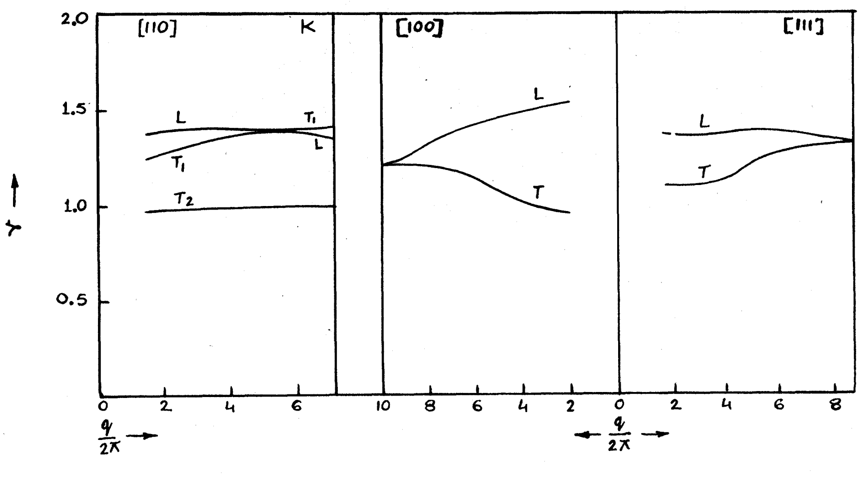

FIG. 3. Calculated Grüneisen parameters for potassium in [100], [110], and [111] directions; $q/2\pi$ is in units of $1/10a$.

It also has an additional advantage of bringing a compromise between the attractive and the repulsive terms as they tend to cancel each other at high wave vectors, as demanded by theory and also proved quite generally by Austin, Heine, and Sham.[15] As already reported in our earlier papers, we have taken $\rho = \gamma_c$ in our calculations because of the arbitrary nature of the parameters. The two remaining unknown parameters $\beta$ and $\gamma_c$ were determined by fitting them in the pseudopotential to reproduce selected measured phonon frequencies. The values of the model parameters are given in Table I.

The volume dependence of the normal modes is described by the one-phonon Grüneisen parameter defined by

$$\gamma_q = -\frac{d\ln\omega_q}{d\ln\Omega_0}. \qquad (3)$$

We have calculated the Grüneisen parameters in the three symmetry directions following Toya's method.[16] With the parameters given in Table I, the Grüneisen parameters were calculated to an accuracy of 1% for alkali metals for 87 reciprocal wave vectors in a $\frac{1}{48}$ part of the first zone.

### III. RESULTS AND DISCUSSION

The calculated values of spin paramagnetism are presented in Table II along with the observed values of Schumacher and Slichter[17] and Schumacher and Vehse[18] and the computed values of Glasser.[19] As is evident from this table, the theoretical and the experimental results for sodium and lithium show a fairly good agreement. In the case of potassium, no experimental results are available, and therefore a comparison could not be made. In particular, our results for lithium are better than those of Glasser.[19]

The one-phonon Grüneisen parameters calculated from the model potential (2) are drawn in Figs. 1, 2, and 3 for lithium, sodium, and potassium, respectively. In general, the pseudopotential calculation leads to Grüneisen parameters of the correct order of magnitude. These quantities are all positive and show considerable variation over the zone. All the calculated $\gamma$ lie in the range ~0.9 to ~1.5 for sodium, ~0.95 to ~1.6 for potassium, and ~0.75 to ~1.6 for lithium. The same order of magnitude was obtained by Wallace[20,21] in his calculation of Grüneisen parameters for alkali metals using Harrison's model pseudopotential. The Grüneisen constant obtained after averaging over a number of frequencies in the three symmetry directions, for alkali metals, is given in Table III along with the observed Grüneisen's constant[22] and computed values by Dugdale and Macdonald[23] and by Wallace.[20] Table III shows that the results are fairly well interpreted by the model potential (2). The Kohn anomalies are not apparent in the Grüneisen-parameter curves and have not been reported in any of

TABLE II. Paramagnetic susceptibility $\chi_p$ for alkali metals. (The value in parentheses is from Ref. 18.)

| Element | Our calculations | Glasser's calculation (Ref. 19) | Experimental value (Refs. 17, 18) |
|---|---|---|---|
| Lithium | 1.74 | 1.33 | 2.08 |
| Sodium | 0.86 | 0.86 | 0.95 (1.13) |
| Potassium | 0.70 | 0.73 | ··· |

TABLE III. Average Grüneisen parameter $\gamma$ for alkali metals.

| Element | Theoretically calculated value | Calculated value of Macdonald and Dugdale (Ref. 23) | Calculated value of Wallace (Ref. 20) | Observed value (Ref. 22) |
|---|---|---|---|---|
| Lithium | 1.11 | ··· | ··· | 1.17 |
| Sodium | 1.16 | 0.86 | 1.18 | 1.25 |
| Potassium | 1.23 | 0.97 | 1.21 | 1.34 |

the experimental phonon dispersion measurements.[24–26] These anomalies are expected to be quite small for alkali metals. The curves are dominated by electrostatic terms and the pseudopotential plays a minor role.

In view of the successful interpretation of the various properties of simple metals,[5–9] this model pseudopotential establishes, in its own right, its importance in the study of lattice dynamics.

## ACKNOWLEDGMENT

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[1] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).

[2] L. J. Sham, Proc. Roy. Soc. (London) A283, 33 (1965).

[3] S. H. Vosko, R. Taylor, and G. Keech, Can. J. Phys. 43, 1187 (1965).

[4] V. Heine and I. Abarenkov, Phil. Mag. 9, 451 (1964).

[5] H. C. Gupta and B. B. Tripathi, Phys. Rev. B 2, 248 (1970).

[6] H. C. Gupta and B. B. Tripathi, J. Chem. Phys. (to be published).

[7] H. C. Gupta and B. B. Tripathi, in Proceedings of the CSIR Annual Convention, Nainital, India (unpublished).

[8] H. C. Gupta and B. B. Tripathi, J. Phys. F 1, 12 (1971).

[9] H. C. Gupta and B. B. Tripathi, J. Chem. Phys. 54, 435 (1971).

[10] V. K. Saxena and D. L. Bhattacharya, Phys. Status Solidi 27, 427 (1968).

[11] R. Abe, Progr. Theoret. Phys. (Kyoto) 29, 23 (1963).

[12] A. B. Migdal, Zh. Eksperim. i Teor. Fiz. 34, 1438 (1968) [Soviet Phys. JETP 7, 996 (1958)].

[13] J. J. Quinn and R. A. Ferrell, J. Nucl. Energy C 2, 18 (1961).

[14] W. A. Harrison, Phys. Rev. 139, A179 (1965).

[15] B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. 127, 276 (1962).

[16] T. Toya, J. Res. Inst. Catalysis Hokkaido Univ. 9, 178 (1961).

[17] R. T. Schumacher and C. P. Slichter, Phys. Rev. 101, 58 (1956).

[18] R. T. Schumacher and W. E. Vehse, J. Phys. Chem. Solids 24, 297 (1963).

[19] M. L. Glasser, Phys. Rev. 134, A1296 (1964).

[20] D. C. Wallace, Phys. Rev. 176, 832 (1968).

[21] D. C. Wallace, Phys. Rev. 178, 900 (1969).

[22] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill, New York, 1939), p. 451.

[23] J. S. Dugdale and D. K. C. Macdonald, Phys. Rev. 89, 932 (1953).

[24] A. D. B. Woods, B. N. Brokhouse, R. H. March, A. T. Stewart, and R. Bowers, Phys. Rev. 128, 1112 (1962).

[25] R. A. Cowley, A. D. B. Woods, and G. Dolling, Phys. Rev. 150, 487 (1966).

[26] H. G. Smith, G. Dolling, R. M. Nicklow, P. R. Vijayraghawan, and M. K. Wilkinson, *Neutron Inelastic Scattering* (IAEA, Vienna, 1968), Vol. I.

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# Kinetics of Two-Photon Absorption from Metastable Defect Levels in Solids

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The results of two-photon absorption from metastable defect levels are presented in terms of a wide range of the characteristic trapping parameters of a simple model of a solid. The instantaneous photocurrent maxima and the luminescence brightness maxima as obtained from exact solutions of the coupled nonlinear kinetic equations are shown to depend on the square of the laser flux, provided that the intensity is a few orders of magnitude smaller than the laser-damage threshold. The square-law dependence is lost close to the threshold. These results are independent of surface recombination and diffusion.

The two-photon absorption rate is proportional to the square of the light intensity ($F$) if the sample is illuminated with monochromatic light (and to the product of the intensities $F_1$, and $F_2$, if two different monochromatic beams are present). Direct measurements of the two-photon absorption rate have confirmed this.[1] Indirect methods based on the square-law dependence have since been taken as strong evidence of the existence of two-photon processes, in for example, luminescence,[1] photocon-