

when their total electronic energy is lowered following an increase in the density of states above the curve for the free electrons. However, the termination of solid solubility is governed by the balance between the free energies of the α phase and of the intermediate phase that follows it and is determined by the common tangent principle.

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Dispersion Curves and Lattice Frequency Distribution of Metals

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A lattice-dynamical 3-constant model for metals is presented. The treatment takes complete account of the symmetry requirements of the lattice. The influence of conduction electrons is considered through the screening of the long-range Coulomb interaction between ions. The theory is used to calculate dispersion curves, frequency spectra, and lattice specific heats of Li, Na, and K. For sodium, good agreement is found with the dispersion curves obtained from measurements of the inelastic scattering of slow neutrons.

INTRODUCTION

THE new method of deducing lattice-dynamical properties from the inelastic scattering of cold neutrons is able to give precise information on frequency spectra and frequency-versus-wave-vector dispersion relations in metals.¹ It is thus of interest to reconsider the theoretical side of this problem.² So far, fitting of experimental curves to theoretical models has met with only moderate success. With simple Born-von Karman models one needs, in general, more parameters than there are elastic constants. The fact that force constants even between more distant neighbors are not negligible points to the existence of long-range forces or to an inadequacy of the models used.

There is clear experimental evidence that the Cauchy relations are not fulfilled for metals. Fuchs has shown³ that this might be explained by the presence of conduction electrons. Their influence on the lattice vibrations was taken into account by De Launay,⁴ who constructed a phenomenological model which includes explicitly the effect of a compressible but shear-free electron gas. His model had some success,⁵ but it violates symmetry requirements, as pointed out, for instance,

by Lax.⁶ In this respect also the new model of Sharma and Joshi⁷ is unsatisfactory.

The same is true for Bhatia's theory,⁸ which essentially considers the electronic effect via the screening of the Coulomb interaction between lattice ions. A theory which includes electronic terms and also takes proper account of the symmetry properties has been developed by Toya.⁹ His model is based on Bardeen's quantum-mechanical calculation of the electron-phonon interaction.¹⁰ Toya's theory is the most fundamental one, but contains a number of electronic parameters which are rather difficult to obtain with good precision. In the case of sodium, agreement between theoretical and experimental^{11,12} dispersion curves is nevertheless quite satisfactory. However, larger discrepancies do appear in the [110] direction.¹³ In the following we propose a theory which is simpler than Toya's and moreover shows good agreement with the experimental dispersion curves of sodium for all observed directions.

¹ *Proceedings of the Symposium on Inelastic Scattering of Neutrons in Solids and Liquids, Vienna 1960, Chalk River 1962* (International Atomic Energy Agency, Vienna, 1961, 1963).

² A preliminary account of this work has been given in *Phys. Letters* **10**, 12 (1964). Equation (1) of that note contains a typographical error in the term M_{xy} . For the correct expression see this paper, Eq. (4).

³ K. Fuchs, *Proc. Roy. Soc. (London)* **A153**, 622 (1935); **A157**, 444 (1936).

⁴ J. de Launay, *J. Chem. Phys.* **21**, 1975 (1953).

⁵ B. Dayal and B. Sharan, *Proc. Roy. Soc. (London)* **A259**, 361 (1960); **A262**, 136 (1961).

⁶ M. Lax, *Proceedings of the International Conference on Lattice Dynamics, Copenhagen 1963*, paper A24 (unpublished).

⁷ P. K. Sharma and S. K. Joshi, *J. Chem. Phys.* **39**, 2633 (1963).

⁸ A. B. Bhatia, *Phys. Rev.* **97**, 363 (1955).

⁹ T. Toya, *J. Res. Inst. Catalysis, Hokkaido Univ.* **6**, 161, 183 (1958).

¹⁰ J. Bardeen, *Phys. Rev.* **52**, 689 (1937).

¹¹ A. D. B. Woods, B. N. Brockhouse, R. H. March, and R. Bowers, *Proc. Phys. Soc. (London)* **79**, 440 (1962).

¹² A. D. B. Woods, B. N. Brockhouse, R. H. March, and A. T. Stewart, *Phys. Rev.* **128**, 1112 (1962).

¹³ The original calculations contain a numerical error, but even correcting for this [R. S. Srivastava and B. Dayal, *Progr. Theoret. Phys. (Kyoto)* **31**, 167 (1964)], there remains still a discrepancy of about 33%.

MODEL

As in Bhatia's theory⁸ we use a model which is based on screened Coulomb interaction between ions, and as in Toya's model⁹ and in agreement with Lax,⁶ the symmetry requirements are taken into account by including umklapp processes. The influence of the electrons is considered through the screening parameter of the Coulomb interaction. The interaction between closed ion shells is included by central interaction between first and second neighbors.

The potential energy of the crystal for small displacements \mathbf{u} of the atoms may be written as¹⁴

$$W = W_0 + \frac{1}{2} \sum_{\mathbf{n}, \mathbf{n}'} W_{\mathbf{n}\mathbf{n}'} \mathbf{u}_{\mathbf{n}} \mathbf{u}_{\mathbf{n}'}. \quad (1)$$

The matrix equation which determines the dispersion relations of the lattice becomes then

$$\left| \sum_{\mathbf{n}} W_{xy}(\mathbf{n}) e^{i\pi \mathbf{q} \cdot \mathbf{n}} - M \omega^2 \delta_{xy} \right| = 0 \quad (2)$$

$$\begin{aligned} [\mathbf{n} &= (2/a)\mathbf{r}_n, \mathbf{r}_n = \text{position vector of atom } n; \\ \mathbf{q} &= (a/2\pi)\mathbf{p}, \mathbf{p} = \text{phonon wave vector;} \\ a &= \text{lattice constant}]. \end{aligned}$$

We split the coefficients W_{xy} into two parts: a short-range closed-shell part S_{xy} and an ionic part I_{xy} .

Shell Part S_{xy}

Restricting our calculation for the moment to bcc lattices we find for the xx element (for central interaction between first and second neighbors)

$$\begin{aligned} \sum_{\mathbf{n}} S_{xx}(\mathbf{n}) e^{i\pi \mathbf{q} \cdot \mathbf{n}} \\ = 8\alpha_1 (1 - \cos\pi q_x \cos\pi q_y \cos\pi q_z) + 4\alpha_2 \sin^2\pi q_x. \end{aligned} \quad (3)$$

α_1 and α_2 are the atomic-force constants for first- and second-neighbor interaction, as for instance defined by Curien.¹⁵ The xy elements are of the form

$$\sum_{\mathbf{n}} S_{xy}(\mathbf{n}) e^{i\pi \mathbf{q} \cdot \mathbf{n}} = 8\alpha_1 \sin\pi q_x \sin\pi q_y \cos\pi q_z. \quad (4)$$

For fcc lattices the corresponding expressions are¹⁶

$$\begin{aligned} \sum_{\mathbf{n}} S_{xx}(\mathbf{n}) e^{i\pi \mathbf{q} \cdot \mathbf{n}} = 4\alpha_1 [2 - \cos\pi q_x (\cos\pi q_y + \cos\pi q_z)] \\ + 4\alpha_2 \sin^2\pi q_x \end{aligned} \quad (5)$$

and

$$\sum_{\mathbf{n}} S_{xy}(\mathbf{n}) e^{i\pi \mathbf{q} \cdot \mathbf{n}} = 4\alpha_1 \sin\pi q_x \sin\pi q_y. \quad (6)$$

Ionic Part I_{xy}

This part arises from the Coulomb interaction between metal ions. The interaction is modified by the

presence of conduction electrons, an effect which gives rise to screening.

The atomic coefficients I_{xy} are defined as second derivatives of the potential ϕ between ions at \mathbf{n} and \mathbf{n}' :

$$I_{xy}(\mathbf{n}) = \partial^2 \phi / \partial x_n \partial x_{n'}. \quad (7)$$

For a screened charge the potential is of the form $r^{-1} \exp(-k_c r)$. Since we are interested in \mathbf{q} space it is convenient to work with the Fourier transform of this potential¹⁷

$$\phi(\mathbf{r}) \propto \sum_{\mathbf{k}} \frac{e^{i\mathbf{k} \cdot \mathbf{r}}}{k^2 + k_c^2}, \quad (8)$$

where the summation should extend over all allowed wave-vector values \mathbf{k} of the electron sea which surrounds the ions.

With $k = (2\pi/a)k'$ and $\mathbf{r} = (a/2)\mathbf{n}$, and replacing the summation by an integration, we find

$$\begin{aligned} \sum_{\mathbf{n}} I_{xy}(\mathbf{n}) \exp[i\pi \mathbf{q} \mathbf{n}] \\ \propto \sum_{\mathbf{n}} \int \frac{k'_x k'_y \exp[i\pi(\mathbf{q} - \mathbf{k}') \mathbf{n}] d\mathbf{k}}{k'^2 + (a/2\pi)^2 k_c^2}. \end{aligned} \quad (9)$$

We now use the known relation

$$\sum_{\mathbf{n}} \exp[i\pi(\mathbf{q} - \mathbf{k}') \mathbf{n}] = \frac{(2\pi)^3}{v_c} \sum_{\mathbf{h}} \delta(\mathbf{q} - \mathbf{k}' + \mathbf{h}), \quad (10)$$

where v_c is the volume of the unit cell and \mathbf{h} is related to the reciprocal lattice vector \mathbf{K} by $\mathbf{K} = (2\pi/a)\mathbf{h}$. This leads to

$$I_{xy}(\mathbf{n}) = A \sum_{\mathbf{h}} \left[\frac{(q_x + h_x)(q_y + h_y)}{|\mathbf{q} + \mathbf{h}|^2 + (a/2\pi)^2 k_c^2} - \frac{h_x h_y}{h^2 + (a/2\pi)^2 k_c^2} \right]. \quad (11)$$

A is a constant which depends on the effective rather than on the valence charge of the ions. The negative second term follows from the condition for translational invariance of the lattice.⁶ In the \mathbf{h} summation, $h_x + h_y + h_z$ has to be even for bcc lattices, and h_x, h_y, h_z have to be all odd or all even for a fcc crystal. k_c is the screening parameter, which in the Thomas-Fermi model is related to the wave vector k_F at the Fermi surface by¹⁷

$$\begin{aligned} k_c(\text{TF}) &= \left[\frac{4 k_F}{\pi a_0} \right]^{1/2} = \left[\frac{4}{\pi} \left(\frac{4}{9\pi} \right)^{1/3} \right]^{1/2} \left(\frac{r_0}{a_0} \right)^{1/2} k_F \\ &= 0.814 (r_0/a_0)^{1/2} k_F. \end{aligned} \quad (12)$$

Here $r_0 = (3/4\pi n_e)^{1/3}$ = interelectronic spacing; n_e = electron density; and $a_0 = \hbar^2/m_e^2 = 0.529 \text{ \AA}$ = Bohr radius.

Applying many-body perturbation theory, Langer

¹⁴ R. A. Smith, *Wave Mechanics of Crystalline Solids* (Chapman & Hall Ltd., London, 1961).

¹⁵ H. Curien, *Bull. Soc. Franç. Minéral. Crist.* **75**, 197 (1952).

¹⁶ C. B. Walker, *Phys. Rev.* **103**, 547 (1956).

¹⁷ D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., Publishers, New York, 1963).

and Vosko¹⁸ were able to show that the screening parameter in a high-density electron gas is not independent of the electron wave number k :

$$k_c^2(\text{LV}) = k_c^2(\text{TF})f(t), \quad (13)$$

where

$$f(t) = \frac{1}{2} + \frac{1-t^2}{4t} \ln \left| \frac{1+t}{1-t} \right| \quad (14)$$

with $t = k/2k_F$. The function $f(t)$ goes to unity for $t \rightarrow 0$ and has a logarithmic singularity at $t = 1$, which gives rise to the so-called Kohn anomalies in the dispersion curves¹⁹ or frequency distribution^{20,21} of metals.

One known shortcoming of the Thomas-Fermi theory is the fact that their model does not adequately take into account the repulsion of the electrons and so overestimates the screening effect. Also, and especially for long wavelengths, this has not yet been improved by the inclusion of the f function. Pines²² has shown that a better parameter should be obtained if one uses, instead of k_c (TF), a value which is about a factor 2 smaller:

$$k_c(P) = 0.353(r_0/a_0)^{1/2}k_F. \quad (15)$$

Combining this with the function $f(t)$ leads then to

$$k_c^2 = k_c^2(P)f(t). \quad (16)$$

The effective potential for large \mathbf{K} values, which corresponds to the core region of the ion, should become very small, since the negative potential energy of an electron near the atomic nucleus is nearly compensated by the high kinetic energy associated with the rapid oscillations of the wave function within the core region.²³ We take this cancellation effect into account by introducing in Eq. (11) a function which is familiar from Wigner-Seitz calculations:

$$g^2(x) = \left[\frac{3(\sin x - x \cos x)}{x^3} \right]^2, \quad (17)$$

where $x = (2\pi/a)r_0|\mathbf{q} + \mathbf{h}|$.

The choice of this function is arbitrary, but it serves the purpose of reducing the influence of larger K values rather well.²⁴ Moreover, Woll and Kohn¹⁹ have shown that the appearance of g^2 is the essential modification of the free-electron result which occurs if one assumes that the electron wave functions are of the Bloch type.²⁵ Including the decay function we thus obtain finally for

the ionic part of the dynamic coefficients

$$I_{xy}(\mathbf{n}) = A \sum_{\mathbf{h}} \left[\frac{(q_x + h_x)(q_y + h_y)}{|\mathbf{q} + \mathbf{h}|^2 + (a/2\pi)^2 k_c^2} g^2(B|\mathbf{q} + \mathbf{h}|) - \frac{h_x h_y}{h^2 + (a/2\pi)^2 k_c^2} g^2(Bh) \right], \quad (18)$$

where $B = (2\pi/a)r_0$.

PARAMETERS AND ELASTIC CONSTANTS

In this section we relate α_1 , α_2 , and A to the three elastic constants of the cubic lattices C_{11} , C_{12} , and C_{44} . This is done by comparing corresponding elements of the dynamical matrix, Eqs. (3) and (4) and also (11), with the equations of elasticity. We obtain the following result for the bcc lattice:

$$\begin{aligned} C_{11} &= (2/a)[\alpha_1 + \alpha_2 + A/a^2 k_c^2], \\ C_{12} &= (2/a)[\alpha_1 + A/a^2 k_c^2], \\ C_{44} &= (2/a)\alpha_1, \end{aligned} \quad (19)$$

and inversely,

$$\begin{aligned} \alpha_1 &= (a/2)C_{44}, \\ \alpha_2 &= (a/2)(C_{11} - C_{12}), \\ A &= (a/2)(C_{12} - C_{44})a^2 k_c^2. \end{aligned} \quad (20)$$

The corresponding result for fcc lattices is

$$\begin{aligned} C_{11} &= (4/a)[\alpha_1 + \alpha_2 + A/a^2 k_c^2], \\ C_{12} &= (4/a)[\alpha_1/2 + A/a^2 k_c^2], \\ C_{44} &= (2/a)\alpha_1, \end{aligned} \quad (21)$$

and inversely,

$$\begin{aligned} \alpha_1 &= (a/2)C_{44}, \\ \alpha_2 &= (a/4)(C_{11} - C_{12} - C_{44}), \\ A &= (a/2)(C_{12} - C_{44})a^2 k_c^2. \end{aligned} \quad (22)$$

CALCULATIONS

As an application of the present theory we have calculated the dispersion curves for the bcc lattices²⁶ of Li, Na and K, using Eqs. (2), (3), (4), (18), (16), and (20). The results are shown in Fig. 1. The elastic constants for Li were taken from Nash and Smith,²⁷ for K and Na from Bender.²⁸ Since in the latter case a large discrepancy exists between experimental values obtained by different authors,^{7,28-30} we have used a C_{44} value (0.554×10^{11} dyn-cm⁻²) which gives good agreement between the experimental (neutron) results¹² and

¹⁸ J. S. Langer and S. H. Vosko, Phys. Chem. Solids **12**, 196 (1959).

¹⁹ E. J. Woll and W. Kohn, Phys. Rev. **126**, 1693 (1962).

²⁰ J. Peretti, I. Pelah, and W. Kley, Phys. Letters **2**, 105 (1962).

²¹ P. L. Taylor, Phys. Rev. **131**, 1995 (1963).

²² D. Pines, Solid State Phys. **1**, 367 (1955).

²³ M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).

²⁴ L. J. Sham and J. M. Ziman, Solid State Phys. **15**, 221 (1963).

²⁵ The same function is also used in the theories of Toya (Ref. 9) and of Sharma and Joshi (Ref. 7). See also the recent paper by W. Cochran, Proc. Roy. Soc. (London) **A276**, 308 (1963).

²⁶ Calculations for the fcc lattice of Cu also show very good agreement with experiment [M. M. Shukla (private communication); Phys. Stat. Solidi **7**, K11 (1964)].

²⁷ H. C. Nash and C. S. Smith, Phys. Chem. Solids **9**, 113 (1959).

²⁸ O. Bender, Ann. Physik **34**, 359 (1939).

²⁹ S. L. Quimby and S. Siegel, Phys. Rev. **54**, 293 (1938).

³⁰ W. B. Daniels, Phys. Rev. **119**, 1246 (1960).

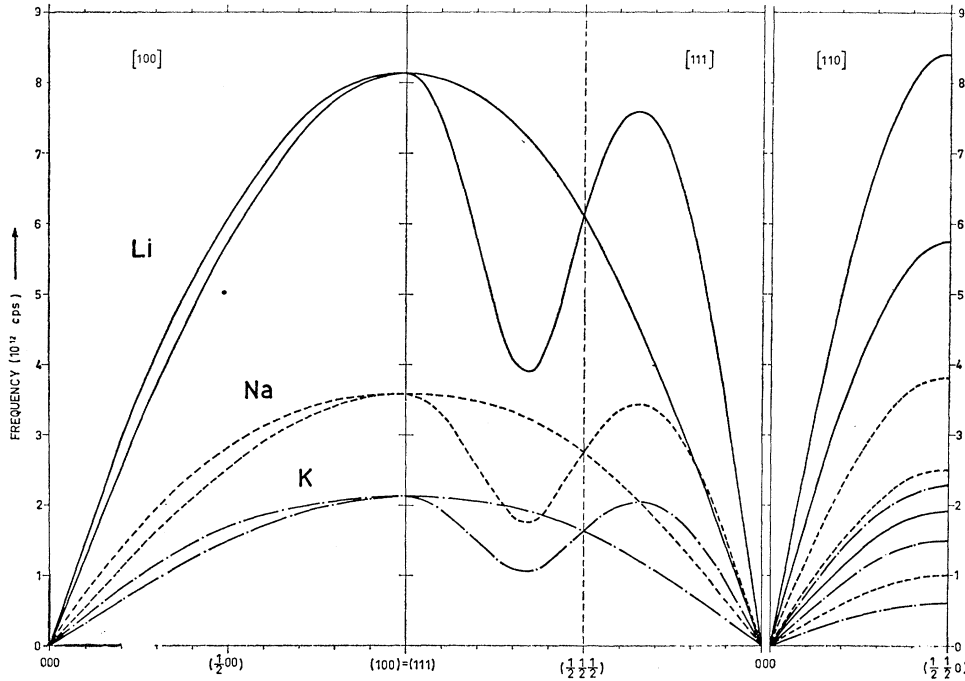


FIG. 1. Dispersion curves for lithium (78°K), sodium (90°K), and potassium (77°K) in the three symmetry directions.

the calculated ones at the point (100) (Fig. 2).³¹ In Fig. 2 we also show a comparison of the results obtained with two different screening parameters, Eqs. (13) and (16). It is obvious that Pines's parameter gives much better agreement with experiment than the curves which are based on the modified Thomas-Fermi model. In all calculations the values for k_F were obtained in the free-electron approximation: $k_F = (3\pi^2 n_e)^{1/3}$ with $n_e = 2/a^3$.

Using the sampling method one can also calculate the frequency spectra from Eq. (2). The results are shown in Fig. 3. These spectra may be introduced into

the formula for the lattice specific heat ($x = h\nu/kT$):

$$C_L(T) = 3R \int_0^{\nu_{\max}} \frac{x^2 e^x}{(e^x - 1)^2} g(\nu) d\nu. \quad (23)$$

The results together with experimental points obtained from calorimetric measurements³² (corrected for $C_p - C_v$) are shown in Fig. 4. The agreement for Na and K is good. The observed discrepancies for Li are probably caused by the application of the free-electron approximation for k_F , or possibly also by a change in crystal structure,

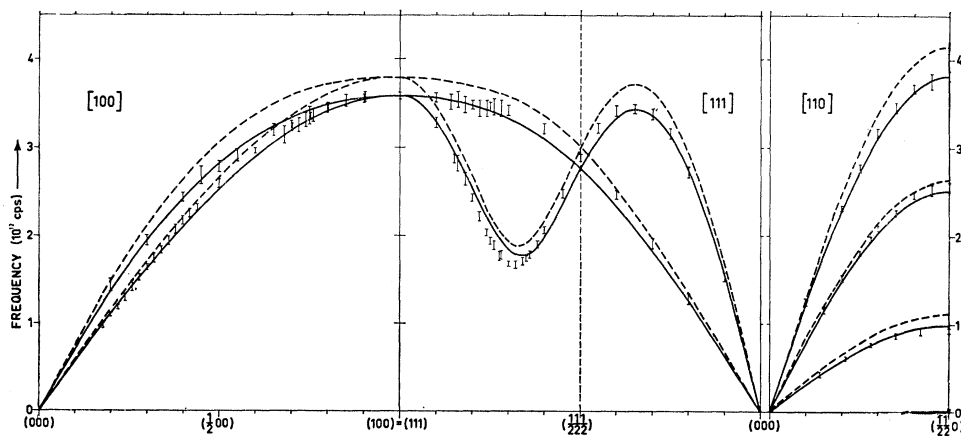


FIG. 2. Comparison of the calculated dispersion curves for sodium at 90°K with experimental results obtained by neutron spectrometry (Ref. 12). Full-line curves are based on the screening parameter of Pines [Eq. (16)]; the dashed ones are calculated with the modified Thomas-Fermi parameter [Eq. (13)].

³¹ Calculations based on the elastic constants as given by Sharma and Joshi lead practically to the same dispersion curves; the agreement for the T branches in the [110] direction is slightly improved.

³² *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1963).

FIG. 3. Lattice frequency spectra of lithium, sodium, and potassium.

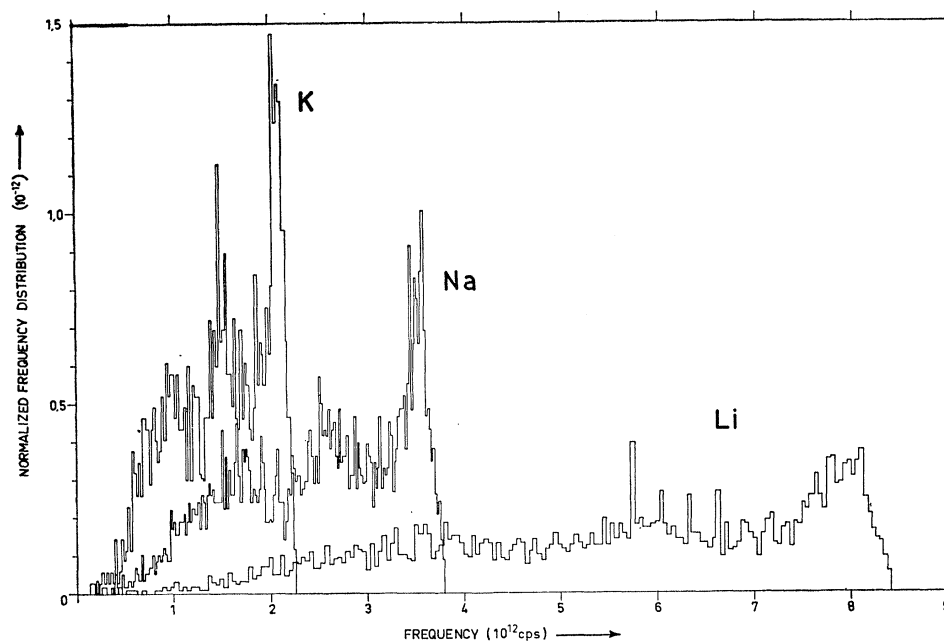
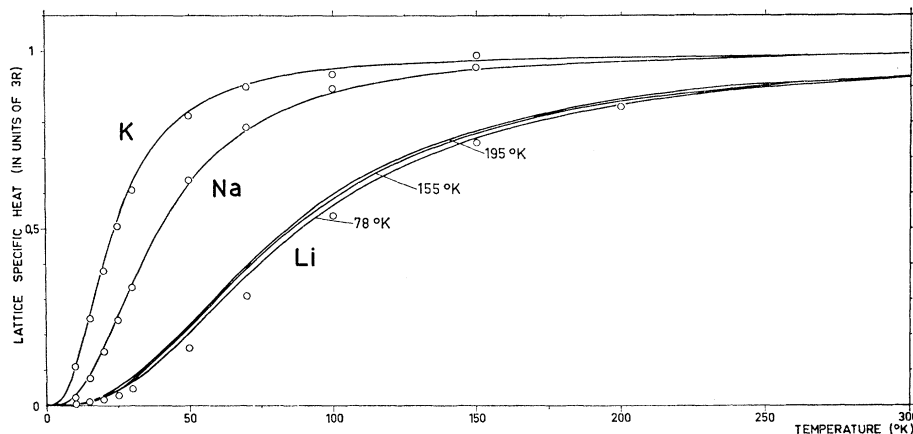


FIG. 4. Comparison of lattice specific heats for Li, Na, and K with experimental calorimetric values. The model parameters for Na and K were calculated from the elastic constants at 90, resp. 77°K. For lithium three sets of parameters were used corresponding to the elastic constants at 78, 155, and 195°K.



which is known to cause an unusual deviation between elastic and calorimetric Debye temperatures.³³

CONCLUSION

From the comparison between experimental and theoretical values, especially for sodium, we conclude that a dynamical model which is based on a "spring" interaction between closed shells together with a Coulomb interaction between shielded effective charges seems to

be quite promising in explaining the lattice-dynamical properties of metals. Two points are obviously essential: the correct choice of the screening length k_e^{-1} (Pines's expression seems to be well suited) and the inclusion of at least the nearest umklapp processes. Moreover, the present model is simple enough, so that a generalization to more complicated metals should be feasible.

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³³ G. A. Alers and J. R. Neighbours, *Rev. Mod. Phys.* **31**, 675 (1959).