Anisotropic Born-Mayer Potential in Lattice Dynamics of Vanadium.

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Summary. — A microscopic theory of the lattice dynamics of the transition metal vanadium is developed based on the Animalu's transition metal model potential (TMMP). The Born-Mayer potential associated with the distribution of the transition metal *d*-electrons is treated as anisotropic. Good agreement with experimental phonon dispersion curves is obtained particularly with regards to symmetry and crossover of longitudinal branches in the [111] direction.

PACS. 63.10. - General theory.

1. – Introduction.

Vanadium is a transition metal that crystallizes as the body-centred cubic (b.c.c.) structure. In the lattice dynamics of vanadium one has to deal separately with the metal ions, the valence or conduction electrons and the interaction between them. This is based on the standard adiabatic and harmonic approximations. The adiabatic or Born-Oppenheimer approximation helps to isolate the various terms that contribute to the total potential energy for the motion of the ions, namely the direct Coulomb interaction between ions, the exchange core (Born-Mayer) repulsion and the ion-ion interaction via the electrons (called the electronic band structure contribution).

Toya[1] first performed a satisfactory calculation for the phonon frequencies in sodium by taking into account the influence of the conduction electrons. He

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[1] J. J. TOYA: *Res. Inst. Catalysis*, **6**, 161, 183 (1958).

used the solution of the electron-phonon problem given by Bardeen [2] which was essentially based on the Wigner-Seitz model [3] of the electron in a metal. The pseudopotential formalism derived from the orthogonalized plane wave (OPW) method by Philips and Klienman [4] and Antoncik [5] and the related Heine-Abarenkov model potential method [6,7] have proved to be convenient and successful tools in the study of the electronic structure and related properties of simple (nontransition) metals. Harrison [8] has given a review of the OPW pseudopotential method. Subsequently, Harrison [9] extended the OPW method to the transition metals but the theory turned out to be quite complicated because of the virtual bound nature of the transition metal d-electrons. It was observed, however, that the augmented plane wave (APW) method [10] explained one-electron energy bands of both nontransition and transition metals quite well [11]. For this reason, Ziman [12], Heine [13] and Hubbard [14] introduced the APW pseudopotential method with a view to describe the transition metals. Later, Animalu [15] and Maclin and Animalu [16] showed how the Heine-Abarenkov model potential can be used to simulate the APW pseudopotential for the transition metals. This approach was called the transition metal model potential (TMMP) method.

Later, Oli and Animalu [17] have shown that there is a significant contribution to the soft modes in the phonon spectrum of vanadium and niobium from s-d hybridization. These arise from the local field corrections to the inverse dielectric matrix associated with the depletion or orthogonalization hole as the resonance ($l = 2$) term in the transition metal model potential method. The

[2] J. BARDEEN: *Phys. Rev.*, **52**, 688 (1937).

[3] E. P. WIGNER and F. SEITZ: *Phys. Rev.*, **43**, 804 (1933).

[4] J. C. PHILLIPS and L. KLEINMANN: *Phys. Rev.*, **116**, 237 (1959).

[5] E. J. ANTONICK: *Phys. Chem. Solids*, **10**, 314 (1959).

[6] V. HEINE and T. V. ABARENKOV: *Philos. Mag.*, **9**, 451, (1964).

[7] A. O. E. ANIMALU and V. HEINE: *Philos. Mag.*, **12**, 1249 (1965).

[8] W. A. HARRISON: *Pseudopotential in the Theory of Metals* (W. A. Benjamin Inc., New York, N. Y., 1966).

[9] W. A. HARRISON: *Phys Rev.*, **131**, 1036 (1969).

[10] J. C. SLATER: *Phys. Rev.*, **51**, 846 (1937).

[11] T. L. LOUCKS: *Augmented Plane Wave Method* (W. A. Benjamin Inc., New York N.Y., 1967).

[12] J. M. ZIMAN: *Proc. Phys. Soc.*, **86**, 337 (1965).

[13] V. HEINE: *Phys. Rev.*, **153**, 674 (1967).

[14] J. HUBBARD: *Proc. Phys. Soc.*, **92**, 921 (1967).

[15] A. O. E. ANIMALU: *Phys. Rev. B*, **8**, 3542 (1973).

[16] A. P. MACLIN and A. O. E. ANIMALU: *Transition Metals*, edited by M. J. G. LEE, J. M. PERZ and E. FAWCETT (1977); A. P. MACLIN and A. O. E. ANIMALU: *Transition Metals 1977*, edited by M. J. G. LEE, J. M. PERZ and E. FAWCETT, Institute of Physics Conference, ser. No. 39(c) (Institut of Physics, Heyden, England, 1978), p. 28.

[17] B. A. OLI and A. O. E. ANIMALU: *Phys Rev. B*, **13**, 2398 (1976).

occurrence of s-d hybridization also affects the Born-Mayer potential[18] through the dependence of this potential[19] on the chemical valence of the transition metal ions and the number of electrons in the outermost shell of neighbouring atoms. For this reason, we wish to explore in this paper the contribution to the occurrence of soft modes from the variation of the chemical valence, assumed for the transition metal ion in determining the effective ion-ion interaction in the crystal, particularly the Born-Mayer potential.

The outline of this paper is as follows. In sect. 2, brief microscopic theory of the lattice dynamics will be presented. In sect. 3, the Born-Mayer contribution will be discussed in order to display its dependence on chemical valence and in sect. 4 the numerical results and conclusions will be discussed.

2. – Microscopic theory of lattice dynamics.

Since vanadium has the simple body-centred cubic lattice structure in its lowest phase, the microscopic theory of lattice dynamics used here is based on the harmonic approximations. Thus the dispersion relation for phonons in the crystal is obtained from the equations

$$(1) \qquad [M\omega\delta_{\alpha\beta} - D_{\alpha\beta}(\boldsymbol{q})]\,\varepsilon_\beta^s(\boldsymbol{q}) = 0 \qquad\qquad (\alpha = 1, 2, 3),$$

where $\boldsymbol{q}$ is the phonon wave vector restricted to the first Brillouin zone; $\varepsilon_\beta^s(\bar{q})$ is the β component ($\beta = 1, 2, 3$) of the unit polarization vector with longitudinal and transverse polarization index s, M is the mass of the ions. $D_{\alpha\beta}$ is the dynamical matrix which is made up of three contributions, viz.

$$(2) \qquad D_{\alpha\beta} = D_{\alpha\beta}^C + D_{\alpha\beta}^R + D_{\alpha\beta}^E,$$

where $D_{\alpha\beta}^C$ is the Coulombic contribution, $D_{\alpha\beta}^R$ is the repulsive core-core contribution, and $D_{\alpha\beta}^E$ is the electronic band-structure contribution. Along the principal symmetry directions (100), (110) and (111) eq. (1) factorizes out and the solutions of the phonon frequencies that are of interest can be expressed as

$$(3) \qquad \omega^2 = \omega_C^2 + \omega_R^2 - \omega_E^2.$$

The theory and the evaluation of the Coulombic contribution ω_C^2 are well known and the results are published for b.c.c. metals[20]. Sham[21] has obtained

[18] M. BORN and J. E. MAYER: Z. Phys., 75, 1 (1932).
[19] F. SEITZ: The Modern Theory of Solids (McGraw-Hill Co., New York, N.Y., 1940).
[20] S. H. VOSOKO, R. RAYLOR and G. H. KEECH: Can. J. Phys., 43, 1187 (1965).
[21] L. J. SHAM: Proc. Phys. Soc., 81, 934 (1963).

the repulsive contribution, $D_{\alpha\beta}^{R}$, due to the overlap between ion core wave functions centred on neighbouring atoms. The electronic contribution, $D_{\alpha\beta}^{E}$, is determined by the indirect interaction between ions via the polarization field of the valence electron gas. This contribution is associated with the electron-phonon interaction matrix which is proportional to the pseudo or model potential carried rigidly by the ions.

3. – The Born-Mayer contribution.

Seitz[22] has given the dependence of the Born-Mayer contribution on the chemical valence through the Born-Mayer potential in the form

$$(4) \qquad V_R(R_{ij}) = b_0 \left(1 + \frac{z_i}{n_i} + \frac{z_j}{n_j} \right) e^{\displaystyle \frac{R_{0i} + R_{0j} - R_{ij}}{\rho}},$$

where $\rho = 0.345 \cdot 10^{-8}$ cm, $b_0 = 0.75 \cdot 10^{-12}$ erg are constants, z_i and z_j are the valences of two interacting ions that have negative signs for electronegative ions, n_i and n_j are the numbers of valence electrons in the outer shells of the ions and equal to eight for all simple ions except L_i in which $n = 2$, R_{0i} and R_{0j} are the ionic radii that are the same for ions[22], while R_{ij} is the separation of the ions.

This may be written for vanadium V^{5+} in the forms

$$(5) \qquad V_R(R_{ij}) = b \exp \left[(2R_0 - R_{ij})/\rho \right],$$

where

$$(6) \qquad b = b_0 \left(1 + \frac{z_i}{n_i} + \frac{z_j}{n_j} \right),$$

and

$$(7) \qquad 2R_0 = R_{0i} + R_{0j}.$$

In the past, Oli and Animalu[17] considered $n_i = n_j = z_i = z_j = 5$, where $b = 2.25 \cdot 10^{-12}$ erg which corresponds to treating the $3d^3 4s^2$ electrons as the outermost atomic shell. However, in reality, the angular distribution of the $3d^3$ electrons (fig. 1a)) is expected to be anisotropic and the radial distribution (fig. 1b)) is expected to have smaller amplitude than the radial distribution of the $4s^2$ electrons. For this reason, we expect in general that $n_i \neq z_j$. In particular, we should have, from fig. 1c) $n_i = n_j = 2$, for the $4s^2$ outermost shells and $z_i = z_j = 5$:

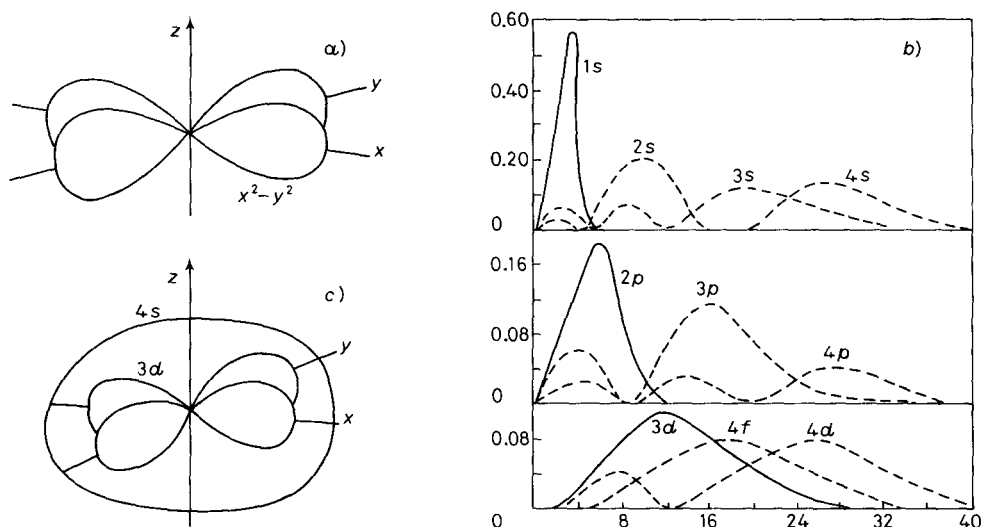[22] R. COLELLA and B. W. BATTERMAN: Phys. Rev. B, 1, 3913 (1970).

Fig. 1. – *a*) Typical spherical harmonic having *d*-type symmetry showing the anisotropic angular distribution of *d*-electrons; *b*) radial probability distribution $\chi^2(nl)$ for several of the lowest levels in hydrogen (abscissa is the radius in atomic units); *c*) 4*s* atomic shell surrounding the inner 3*d* shell, which follows from *a*) and *b*).

this means that the value $b = 2.25 \cdot 10^{-12}$ erg assumed by Oli and Animalu may be replaced by $2b = 4.5 \cdot 10^{-12}$ erg. In practice, if the anisotropy of the local field correction is taken into account in the manner proposed by Oli and Animalu [17], then the degeneracy of the longitudinal branches of the phonon spectrum in the (111) and (100) directions at the zone boundary requires that we take $b = 2.25 \cdot 10^{-12}$ erg in the (100) direction but $b = 4.5 \cdot 10^{-12}$ erg in the (111) and (110) directions.

5. – Numerical results and conclusion.

Phonon dispersion curves along the principal symmetry directions were computed for metallic vanadium within the framework of the transition metal model potential. The calculations have been performed for the lattice spacings at room temperature. The polarization vectors for the b.c.c. structure in this case are $\varepsilon_L = (1, 0, 0)$, $\varepsilon_{T_1} = (0, 1, 0)$, $\varepsilon_{T_2} = (0, 0, 1)$, [1, 0, 0] direction; $\varepsilon_L = (1, 1, 0)/\sqrt{2}$, $\varepsilon_{T_1} = (1, -1, 0)/\sqrt{2}$, $\varepsilon_{T_2} = (0, 0, 1)$, in the [1, 1, 0] direction; $\varepsilon_L = (1, 1, 1)/\sqrt{3}$, $\varepsilon_{T_1} = (1, -1, 0)/\sqrt{2}$, $\varepsilon_{T_2} = (1, 1, -2)/\sqrt{6}$ in the [1, 1, 1] direction.

The total phonon frequency is of the form

$$(8) \qquad\qquad w^2 = w_C^2 + w_R^2 - w_E^2 - w_{lc}^2,$$

where w_{lc}^2 is the local-field correction that is generated from the electronic contribution. The theoretical calculation of the phonon spectrum of vanadium is compared with the experimental data of Colella and Batterman[11] displayed in fig. 2. The agreement is quite good.
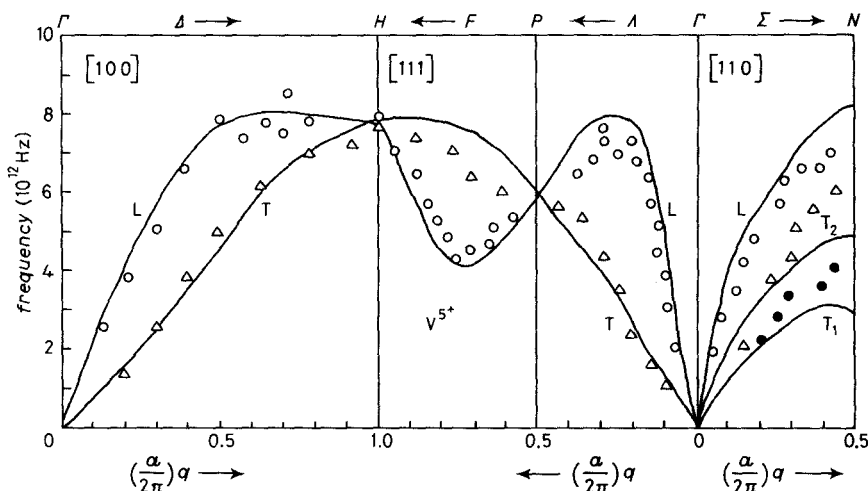

Fig. 2. – Calculated (continuous curves) and measured[22] phonon spectrum of b.c.c. vanadium including anisotropic Born-Mayer contribution.

In this paper, we have investigated the occurrence of soft modes through the Born-Mayer potential in so far as the potential depends on the occupancy of the $3d$ and $4s$ shells. A particularly important result of our present investigation is the more careful determination of the dependence of the Born-Mayer potential on the chemical valence and the number of electrons in the outermost atomic shell as discussed in sect. 3, and the necessity to treat the Born-Mayer potential as anisotropic on the basis of symmetry considerations.

● RIASSUNTO (*)

Si sviluppa una teoria microscoopica della dinamica reticolare del metallo di transizione vanadio basato sul modello di potenziale di transizione metallico (TMMP) di Animalu. Il potenziale di Born-Mayer associato con la distribuzione degli elettroni d dei metalli di transizione è trattato come anisotropico. Si ottiene un buon accordo con le curve sperimentali di dispersione dei fononi particolarmente riguardo alla simmetria e l'incrocio delle ramificazioni longitudinali nella direzione [111].

(*) Traduzione a cura della Redazione.

Анизотропный потенциал Борна-Майера для описания динамики решетки ванадия.

Резюме (*). — Развивается микроскопическая теория динамики решетки переходного металла ванадия, которая основана на модельном потенциале Анималу для переходного металла. Потенциал Борна-Майера, связанный с распределением d-электронов в переходном металле, является анизотропным. Что касается симметрии и кроссовера продольных ветвей в направлении [111], получается хорошее согласие с экспериментальными дисперсионными кривыми фононов.

(*)   *Переведено редакцией.*