Model for Lattice Dynamics in Metals

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A new model is proposed for the calculation of dispersion curves in metals. The conduction electrons are taken into account with the Thomas-Fermi interaction. In this model, the requirements of symmetry are satisfied and no external forces are needed in order to maintain static equilibrium.

IT has been possible with the Born–von Kármán (BvK) model[1] to account for a large number of experimental data on specific heat, infrared absorption, neutron scattering, etc. The theory seems to apply well to nonmetallic crystals; however, for metals there is a special problem. The conduction electrons, which are more or less free to move in the metal are not taken into account in this model. Fuchs[2] has shown that these free electrons are responsible for the violation of the Cauchy relations which are implied in the BvK model.

Many authors[3] have proposed modifications to the BvK model in order to take into account the effect of the conduction electrons. The model assumed by these authors was that of a continuous medium, the electron cloud, into which the lattice was immersed.

The results obtained from these calculations still were at variance with experiment. For example, the dispersion curves obtained directly from thermal neutron scattering[4] could not be reproduced. Lax[5] has shown that the inadequacy of this approach was due to the fact that the translational invariance of the lattice was not taken into account.

More recently, Krebs[6] proposed a model which takes into account the remarks of Lax. In addition to the BvK, he uses a long range interaction of the ions, using a screened Coulomb potential. The theoretical dispersion curves are in good agreement with experiment. This model, however, suffers from a serious drawback: The derivative of the screened Coulomb interaction energy is not zero at equilibrium as it is for the BvK term. This result implies that external forces must be applied to maintain the system in equilibrium. This result has been pointed out by Cochran.[7]

The model we propose satisfies the requirement of translational invariance and is in equilibrium without recourse to external forces. In this model, the ionic part of the interaction is taken to be the first two terms in a Taylor expansion of the potential energy. The first two derivatives of the potential energy are considered as parameters (α and β, respectively), as in the model of Bahtia.[8]

A third parameter (γ) comes from the electronic part and can be shown to be the bulk modulus of the electron gas. For this interaction, the linearized Thomas-Fermi equation is used and Poisson's equation is solved for the whole crystal in order to preserve the symmetry of the lattice.

The equation[9] of motion can then be written as

$$\rho\omega^2\mathbf{e}=\sum_{\substack{\mathbf{l}\\ \text{neighbors}}}(4/l^2)[\sin^2\tfrac{1}{2}(\mathbf{l}\cdot\mathbf{q})][(\alpha/l^2)\mathbf{l}\cdot(\mathbf{l}\cdot\mathbf{e})+\beta\mathbf{e}]$$
$$+\frac{4\pi Q^2}{v_c^2}\sum_{\mathbf{q}}\left\{\frac{[(\mathbf{q}+\mathbf{g})\mathbf{e}](\mathbf{q}+\mathbf{g})}{|\mathbf{q}+\mathbf{g}|^2+\lambda^2(|\mathbf{q}+\mathbf{g}|)}-\frac{(\mathbf{g}\cdot\mathbf{e})\mathbf{g}}{g^2\times\lambda^2(g)}\right\},$$

where $\mathbf{l}$ is the distance of the nearest neighbors from the origin, $\mathbf{e}$ is the unit vector of the displacement of the ion at the origin, $\mathbf{q}$ is the wave vector of the phonon, $\mathbf{g}$ is the vector in the generalized reciprocal lattice, v_c is the volume of a cell in the lattice, $\lambda(k)$ is the Thomas-Fermi parameter, as modified by Langer and Vosko,[10] Q is the charge of the ion, ρ is the density of the metal. Let $\gamma=4\pi Q^2/v_c^2\lambda^2(0)$, then at the limit $\mathbf{q}\to 0$, we have

$$\text{bcc lattice}\quad \alpha=-(9/16)(C_{11}-C_{12}-2C_{44}),$$
$$\beta=(3/16)(C_{11}-C_{12}),$$
$$\gamma=C_{11}-C_{44};$$
$$\text{fcc lattice}\quad \alpha=-C_{11}+C_{12}+2C_{44},$$
$$\beta=(1/4)(C_{11}-C_{12}-C_{44}),$$
$$\gamma=2C_{11}-C_{12}-3C_{44}.$$

Moreover, the equilibrium condition $\partial V/\partial r|_l=0$ gives us a relation from which we can deduce the lattice constant.

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The discrepancy in the Cauchy relations is given by

$$C_{12}-C_{44}=\gamma-(16/3)\beta, \quad \text{for bcc}$$
$$=\gamma-8\beta, \quad \text{for fcc.}$$

Thus, not only does our model take into account the effect of the free electrons on the Cauchy relations but it also provides for the modification of internal equilibrium due to the electron gas. In fact, without free electrons we must have $\beta=\partial W/\partial r$ (short range)$=0$.

Thus, this result is in agreement with Fuchs's calculations of the Cauchy relations.

We are doing calculations with this model for various metals and the results will be published elsewhere. The results seem to be in good agreement with experiment.

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Photoemission and Optical Studies of the Electronic Structure of Palladium*

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Photoemission and optical-reflectivity measurements have been carried out on palladium samples prepared and measured in vacuum of approximately 5×10^{-9} Torr for $h\nu\leq11.8$ eV. In addition, photoemission measurements were made on Pd samples in poorer vacuum for $h\nu=16.8$ and 21.3 eV. The optical functions ϵ_1, ϵ_2, $\omega\sigma$, α, and $\mathrm{Im}(1/\epsilon)$ have been calculated from reflectivity data by Kramers-Kronig analysis. Optical transitions are found to be predominantly nondirect in the spectral range studied, although relatively weak direct (or nonconstant-matrix-element) transitions are also observed for 11.8 eV$>h\nu>$9.8 eV. The valence-band optical density of states of Pd, deduced from photoemission and reflectivity data, has peaks at $E-E_f=-0.1$ and -1.1 eV and is lacking in strong structure elsewhere. There is no evidence for a high density of states near $E-E_f=-5$ eV as in Ni, Co, Fe, and Cr. The d-band structures in Pd and Ag are found to be related rather well by the rigid-band model. Values for the density of states at the Fermi energy in Pd are obtained, and are found to be in reasonable agreement (within experimental accuracy) with values obtained from band calculations. A strong peak in the loss function obtained from reflectivity data is observed at $h\nu=7.5$ eV. This correlates with the strong peak observed at 6.8 eV in energy-loss measurements and is probably due to plasma resonance. Detailed analysis of the photoemission and optical data indicate that a peak in the energy-distribution curves, which appears 7.5 eV below the maximum energy in the energy distributions for $h\nu=18.6$ and 21.3 eV, is due to electrons scattered by this plasma resonance.

I. INTRODUCTION

FROM photoemission and optical studies it has been possible to obtain the optical density of states of a number of transition and noble metals. The optical densities of states of the $3d$ ferromagnetic metals—Fe,[1] Co,[2] and Ni[3]—all have a strong peak at about 5 eV below the Fermi level. Recent work by Lapeyre[4] indicates a peak in Cr near 5 eV but weaker in intensity than that in the ferromagnetic transition metals. The paramagnetic metal palladium lies directly below Ni in the periodic table and from band theory its electronic structures would be expected to be similar to that of Ni. If the anomalous peak is associated with ferromagnetism in the $3d$ transition metals, it should not appear in Pd.[5] Therefore, experimental data on the electronic structure of Pd over a wide energy range (~10 eV) are of considerable interest. In this paper, photoemission and optical-reflection data on Pd are presented and the optical density of states determined. These results are discussed in terms of its electronic structure. Results on Pt will be presented in subsequent papers.

II. EXPERIMENTAL METHODS

Photoemission and optical-reflectivity measurements were made on Pd samples prepared and kept in a continuously pumped (oil-free, VacIon system) stainless-steel chamber (pressure during measurement was about 5×10^{-9} Torr). Two methods of sample preparation were used: evaporation by e-gun evaporator and heat cleaning in high vacuum. In the e-gun evaporator (manufactured by Varian Associates), the evaporant (99.99% pure, obtained from Electronic Space Products, Los Angeles), placed on a water-cooled crucible, was evaporated by electron-beam bombardment. The

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