Angular forces and normal vibration in nickel

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Normal modes of vibration of nuclei in fcc nonmonovalent transition-element nickel have usually been investigated by lattice-dynamical approaches in which the Cauchy discrepancy ($C_{12} - C_{44}$) has been attributed to the bulk modulus of the conduction electrons (i.e., $C_{12} - C_{44} = K_e$). The authors consider here an approach in which it is assumed that there are also noncentral-force contributions that combine with the electron gas to break the Cauchy relations of elasticity. For this purpose, the angular interactions are taken from the Clark, Gazis, and Wallis approach and volume forces have been taken from the Krebs scheme, using an appropriate value of the screening parameter taken from the Bohm-Pines plasma theory which takes into account the electron correlations. The frequency versus wave-vector dispersion relations along symmetry directions [$\zeta 00$], [$\zeta\zeta 0$], and [$\zeta\zeta\zeta$] in the reciprocal space of Ni are computed from the solutions of the secular equation along these directions. The frequency distribution has been calculated with the Blackman's root-sampling technique for a discrete subdivision in wave-vector space. Below $\Theta/10$, where the sampling technique gives an inadequate description of the normal modes of vibrations, a modified Houston's spherical six-term integration procedure is employed. Results obtained with the above combination of various interactions are discussed in the light of previous calculations, and the present values are found to yield comparatively better agreement with experiments.

I. INTRODUCTION

In a quantum-mechanical treatment of the elastic constants of monovalent metals, Fuchs[1] found that the extensional elastic constants C_{11}, C_{12}, and the bulk modulus $\frac{1}{3}(C_{11} + 2C_{12})$ involved the same central forces as the shear constants plus a volume-dependent part due to the kinetic and potential energies of the electron gas. Therefore, instead of the Cauchy relations $C_{12} = C_{44}$ of central-force cubic lattices, one should have $C_{12} - C_{44} = B_e$ as discussed by De Launay[2] (where B_e is the bulk modulus of valence electrons). However, this concept ($C_{12} - C_{44} = B_e$) is valid only for an essentially spherical Fermi surface and will not hold for multivalent cases. If we overlook the fact that the approximate concept, $C_{12} - C_{44} = B_e$, which arises out of Fuch's work, may be a too simple and too poor an approximation, we must naturally consider noncentral forces to be partially responsible for the deviation from the Cauchy relation. Such a noncentral character could originate from the nonsphericity of the $3d$ charge distribution.[3,4] We know that the cubic field in metals removes the fivefold degeneracy and destroys the sphericity of the $3d$-band electrons and that the d-band charge distribution gives rise to noncentral interatomic forces,[3,4] but the main question is to examine whether these forces are significant in magnitude. Gupta and Tripathi[3] recently considered the influence of angular forces on the crystal dynamics of noble metals and it emerged that the contribution of the angular-noncentral-force interaction is nearly 10% that of the central one. Thus it may be inferred that these interactions play an important

role in the lattice-dynamical description of fcc structures.

The lattice dynamics of Ni has been investigated by several workers,[5-7] but the study has been mostly confined to phonon dispersion only. It is evident that almost every model gives a good fit to experiments only for small values of the phonon wave vector. In these calculations the results achieved with the De Launay[2] and Sharma and Joshi[5] models are open to question. Unfortunately, as pointed out by Lax,[8] these schemes violate the symmetry requirements of the lattice. Though the calculations assuming Krebs' idea[9] consider the above requirement, the model neglects completely the influence of angular vibrations on the crystal dynamics of solids. From previous work[3] it is evident that they are important and it is therefore suicidal to think that such interactions are too insignificant in magnitude to cause theoretically measurable effects. In this direction, the recent statement of Upadhyaya[10] regarding angular forces appears to be inadequate. The discrepancy of various theories[5-7] with experiment at higher values of (reduced wave vector) ζ cannot be attributed to the long-range nature of forces in the case of Ni due to the fact that in this crystal the short-range interaction is by far the most important one.[6] Indeed, the elastic constant C_{44} which determines to a large extent the magnitude of the short-range interactions is much higher for Ni than for other fcc metals, whereas the deviation from the Cauchy relation which affects the magnitude of the long-range interaction is comparatively small. Moreover, the earlier calculations[6] have demonstrated clearly that the consideration of the elec-

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tron-ion matrix element does not affect the phonon spectrum of Ni to a great extent. Therefore, we must look for an additional interaction (i.e., angular) so as to get a better fit with experiments. In the present paper we report a calculation of the lattice dynamics of Ni in which the deviation from the Cauchy relation is considered to arise from angular interactions in addition to the usual central and volume forces. The angular forces are taken from the Clark, Gazis, and Wallis (CGW) model[11] and the volume forces are borrowed from Krebs.[9] A similar approach has already been followed by Shukla et al.[12] and the present authors[13] to study the various dynamical properties of cubic crystals.

II. MODEL

The system in which the vibrations take place consists of point ions having their equilibrium positions at the lattice points and an electron gas surrounding the ions. The assumption of point ions is valid for most of the simple[14] and cubic transition metals[15] excepting group-IB metals. The phonon frequencies in the harmonic approximation are given by the secular equation

$$|D_{\mu\nu}(\vec{q}) - M\omega^2_{\vec{q},i}\delta_{\mu\nu}| = 0 , \tag{1}$$

where

$$D_{\mu\nu}(\vec{q}) = D^{i\text{-}i}_{\mu\nu}(\vec{q}) + D^{i\text{-}e}_{\mu\nu}(\vec{q}) .$$

Here $D_{\mu\nu}(\vec{q})$ are the elements of the dynamical matrix, $\vec{q}$ is the wave vector confined to the first Brillouin zone (BZ), M is the mass of the ion, and $\omega_{\vec{q},i}$ is the normal-mode frequency of wave vector $\vec{q}$ and branch index i.

$$D_{11} = 2\left(\alpha + \frac{8}{a^2}(\gamma_1 + \gamma_2)\right)[2 - C_1(C_2 + C_3)] + 4\beta s_1^2 - \frac{\gamma_1}{a^2}(2\cos aq_1 - \cos aq_2 - \cos aq_3)$$

$$+ A\sum_{\vec{G}}\left(\frac{(\vec{q}+\vec{G})_1(\vec{q}+\vec{G})_1}{|\vec{q}+\vec{G}|^2 + k_c^2} g^2(|\vec{q}+\vec{G}|r_0) - \frac{G_1^2}{G^2 + k_c^2}g^2(|\vec{G}|r_0)\right), \tag{2}$$

$$D_{12} = \left(2\alpha - \frac{16\gamma 1}{a^2}\right)s_1 s_2 + A\sum_{\vec{G}}\left(\frac{(\vec{q}+\vec{G})_1(\vec{q}+\vec{G})_2}{|\vec{q}+\vec{G}|^2 + k_c^2}g^2(|\vec{q}+\vec{G}|r_0) - \frac{G_1 G_2}{G^2 + k_c^2}g^2(|\vec{G}|r_0)\right). \tag{3}$$

In the above equations α, β and γ_1, γ_2 are central and angular force constants taken up to second neighbors, r_0 is the radius of the Wigner-Seitz sphere, the electronic force constant is written as $A = K_e v_c k_c^2$, where $K_e = 4\pi e^2 Z_m Z_n/v_c^2 k_c^2$ is the bulk modulus of the electron gas. The $g^2(x)$ function known as the overlap integral or interference factor follows from the Wigner-Seitz model for the band structure and is given by

$$g^2(x) = \left(\frac{3(\sin x - x\cos x)}{x^3}\right)^2 .$$

Equations (2) and (3) involve summation over all the reciprocal-lattice vectors $\vec{G}$ which are obtained from the structure of the crystal. $C_1 = \cos(\frac{1}{2}aq_1)$, $s_1 = \sin(\frac{1}{2}aq_1)$, k_c is the Bohm-Pines[16] screening parameter which is given by

$$k_c^2 = k_{c(BP)}^2 f(t), \tag{4}$$

$$k_{c(BP)} = 0.353(r_0/a_0)^{1/2}k_F ,$$

$$f(t) = \frac{1}{2} + \frac{1-t^2}{4t}\ln|(1+t)/(1-t)| ; \quad t = k/2k_F .$$

Here a_0 is the Bohr radius. In the calculations the value of k_F is defined in the free-electron approximation with $k_F = (3\pi^2 n_e)^{1/3}$, where $n_e = 2.4/a^3$ for Ni assuming only 0.6 conduction electrons per atom. This is reasonable since in Ni ten electrons have to be distributed over the 3d and 4s bands, and since the value of the magnetic moment indicates that there are 0.6 holes per atom in the 3d band.[17] The function $f(t)$ goes to unity for $t \to 0$ and has a logarithmic singularity at $t = 1$. In Eqs. (2) and (3) the electron-ion interaction part of the dynamical matrix in the limit of very long waves produces an additive stiffness for the longitudinal modes without affecting the transverse ones. It is analogous to the procedure adopted by Bhatia,[18] de Launay,[2] and Sharma and Joshi[19] to explain the Cauchy discrepancy in cubic metals. In the long-wavelength limit the force constants involved in the dynamical matrices of fcc metals can be related to

the measured elastic constants and the two zone-boundary frequencies. The resulting expressions are

$$aC_{11} = 2\alpha + 4\beta + 32\gamma_1/a^2 + 16\gamma_2/a^2 + 4A/a^2k_c^2 ,$$

$$aC_{12} = \alpha - 16\gamma_1/a^2 - 8\gamma_2/a^2 + 4A/a^2k_c^2 ,$$

$$aC_{44} = \alpha + 8\gamma_2/a^2 , \qquad\qquad (5)$$

$$\pi^2 m \nu_T^2 = \alpha + 8\gamma_1/a^2 + 8\gamma_2/a^2 ,$$

$$\pi^2 m \nu_L^2 = 2\alpha + \beta + 8\gamma_2/a^2 + AC .$$

ν_L and ν_T represent the longitudinal and transverse zone-boundary frequencies in the $[\zeta\zeta\zeta]$ and $[\zeta 00]$ directions: C is the electronic contribution at the zone boundary in the $[\zeta\zeta\zeta]$ direction. The electronic contribution at the zone boundary of the transverse branch in the $[\zeta 00]$ direction has been neglected owing to it being very small. The effect of this contribution is found to be negligible on integrated properties. The solutions of Eqs. (5) determine the unknown force constants in terms of elastic constants and zone-boundary frequencies. The calculated force-constant values are given in Table I. These force constants are substituted to find the roots (frequencies) of the secular determinant for selected values of phonon wave vectors.

III. NUMERICAL COMPUTATION

The frequency distribution function has been calculated with the Blackman root-sampling technique for a discrete subdivision in wave-vector space. The only wave vectors of interest are those lying within the first Brillouin zone. This method can give an accurate spectrum when the number of frequencies falling in a small frequency interval is fairly large. In order to get a fairly large number of frequencies the translation vector of the reciprocal space was divided into 20 equal parts so as to get a grid of 8000 equally spaced points inside

TABLE I. Calculated force constants of nickel.

Parameters calculated	Nickel
α (10^3 dyn/cm)	31.4030
β (10^3 dyn/cm)	0.8657
γ_1 (10^3 dyn/cm)	−0.7502
γ_2 (10^3 dyn/cm)	1.5277
A (10^3 dyn/cm)	44.0378

the first Brillouin zone. Since a number of points in the first Brillouin zone are symmetrically equivalent, vibration frequencies are calculated at points lying within the irreducible trihedral angle of the reciprocal space of a cubic crystal. For sampling purposes, the number of frequencies falling into a certain frequency interval are counted and from these values a frequency distribution is plotted which is drawn with arbitrary unit for $G(\nu)$. After obtaining the frequency distribution, the lattice specific heat at constant volume, C_v, can be computed from the following relation:

$$c_v = k_B \int_0^{\omega_m} G(\omega) \frac{x^2 e^x}{(1 - e^x)^2} d\omega , \qquad (6)$$

where $x = \hbar\omega/k_B T$, k_B is the Boltzmann constant, ω is the vibration frequency of the phonons, and $\hbar$ is Plank's constant divided by 2π. The sampling technique was used at moderate temperatures down to $\frac{1}{10}\Theta$ since $G(\nu)$ calculated by this method can not be very accurate in the low-frequency range and because of the coarseness of the mesh in the vicinity of the origin. Below $\frac{1}{10}\Theta$, C_v has been calculated from the following relation:

$$C_v = k_B \frac{v}{(2\pi)^3} \sum_p \int_0^{q_m} \int_\Omega E(x)q^2 \, dq \, d\Omega . \qquad (7)$$

Here v is the crystal volume, p is the polarization vector, Ω is the solid angle in wave-vector space, and $E(x)$ is the Einstein specific-heat function given by $E(x) = x^2 e^x/(1 - e^x)^2$. In evaluating C_v from Eq. (7) the integration over $\vec{q}$ is performed numerically and the integration over the solid angle Ω is carried out by using the modified Houston spherical six-term integration procedure[20] as elaborated by Betts et al.[21] In this method the integrand which is invarient under the operations of the complete cubic symmetry group is expanded in Kubik harmonics and the series is averaged analytically over the complete solid angle. The use of Houston's method for evaluating the integral

$$J = \int I(\theta, \phi) \, d\Omega$$

by a six-term approximation leads to the formula

$$J = \frac{4}{1081080}\pi(117\,603I_A + 76\,544I_B + 17\,496I_C$$
$$+ 381\,250I_D + 311\,040I_E$$
$$+ 177\,147I_F).$$

The subscripts A, B, C, D, E, and F refer to the values of the integrand $I(\theta, \phi)$ along the directions [100], [110], [111], [210], [211], and [221], re-

spectively. The dynamical matrix giving the angular frequencies for the normal modes of lattice vibrations is solved for these symmetry directions and the solutions are used for the evaluation of the integral over q.

IV. RESULTS AND DISCUSSION

Birgeneau et al.,[22] and Dewit and Brockhouse[23] have measured experimentally the frequencies of the normal modes of lattice vibrations in nickel at 296 °K along the major symmetry directions, using the technique of neutron spectroscopy. However, the above observed data are not in good agreement with the time-of-flight measurements of Houtecler and Van Dingenen,[24] especially near the zone boundary. These discrepancies could not be accounted for by normal experimental errors, so a reasonable explanation is still lacking; tentatively, this could be attributed to an incorrect subtraction of the socle under the high-energy one-phonon peaks. For comparison, the experimental points from the observations of Birgeneau et al. and Hautecler and van Dingenen are plotted in Fig. 1 along with the theoretical curve calculated from our assumed approach. To test the usefulness of this approach, it is of interest to compare our present computations with those calculated by earlier workers,[5,6,7] using various approximations and theories to calculate the phonon spectra of Ni. Basically, all

these approaches are simply an extension of the Born–von Kármán's phenomenological approach which is correct within well-defined and reasonably good approximations yielding a set of interatomic force constants having a direct intuitive significance and, therefore, of interest. It is evident that both the Krebs[9] and the CGW[11] schemes agree with each other's results. As compared to other models, our results are comparatively in much better agreement with the observations. Since the present scheme represents a modification of both the Krebs and the CGW models, this study is especially interesting for these approaches. However, as far as the CGW scheme is concerned, it was originally developed by Clark, Gazis, and Wallis to study surface physics and therefore no attempt was made to incorporate the influence of valence electrons on the ionic lattice. The information extracted from De Launay's model[2] shows disappointing agreement with experiments.

Tchernoplekov et al.[25] and Mozer et al.[26] have used the incoherent-inelastic-neutron-scattering techniques to measure directly the frequency distribution function of nickel. Birgeneau et al.[22] have also calculated the frequency spectrum of nickel within the Born–von Kármán theory by fitting four-neighbor force constants to their experimental phonon dispersion curves obtained from inelastic scattering of neutrons at 296 °K. In Fig. 2 we have shown the experimentally measured
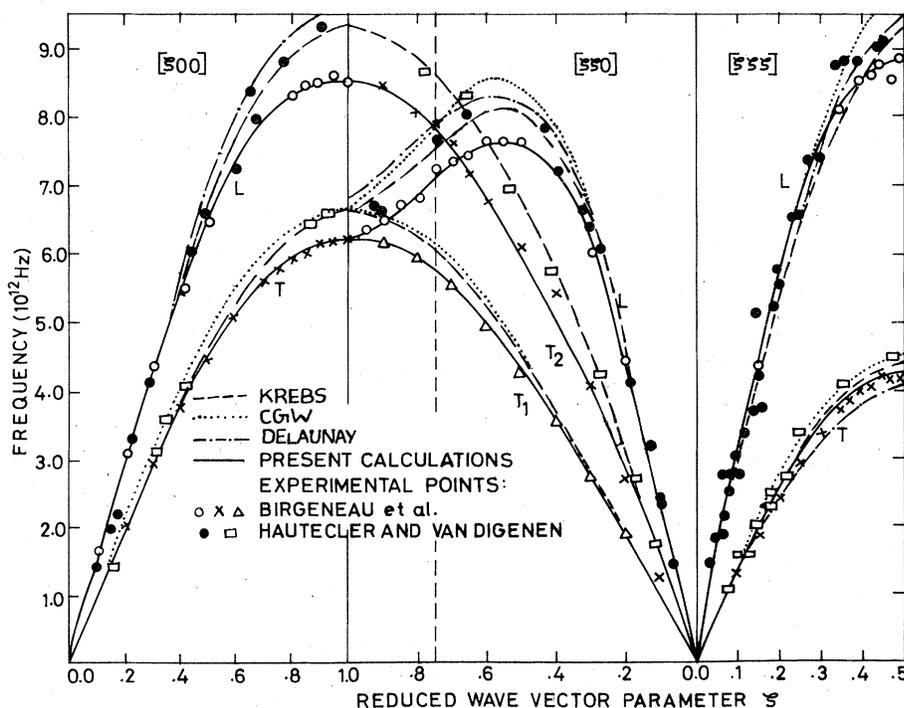

FIG. 1. Phonon dispersion curves for nickel along the symmetry directions.
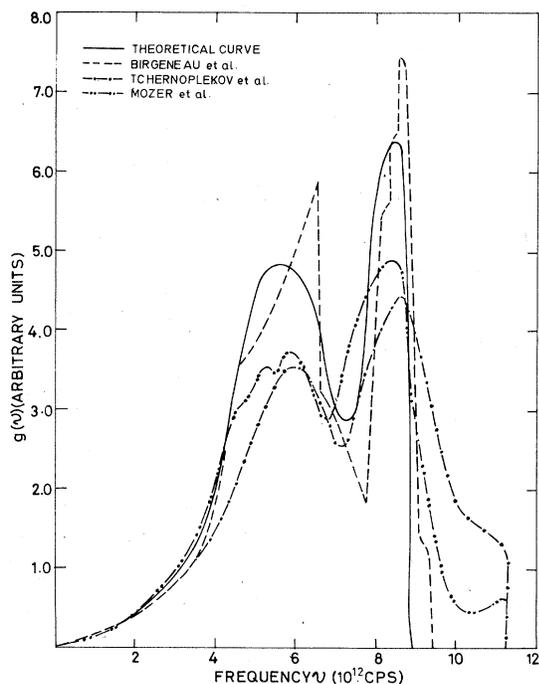
FIG. 2. Frequency spectrum of nickel.

FIG. 3. Debye temperature of nickel as a function of temperature.

curves[22,25,26] along with our theoretical one. Ex-
perimental specific heats of nickel have been re-
ported by Eucken and Werth[27] and later on similar
observations of this crystal have also been carried
out by Busey and Giauque.[28] Measurements of the
latter authors are in close agreement with the re-
sults of Eucken and Werth in the whole tempera-
ture range considered for the experimental study
of specific heats of nickel. Results of both these
groups extend almost up to the same range of tem-
perature and are plotted in Fig. 3 along with our
theoretical curve. Since the specific heat is very
insensitive to the details of the spectrum, calcula-
tions have been compared with experiments in
terms of the equivalent Debye temperature Θ
which is perhaps the most sensitive property to
test the validity of any approach. In order to es-
timate the lattice specific heat, the electronic and
spin-wave contributions have to be subtracted
from the experimental heat capacities. The coef-
ficient of the electronic specific heat of nickel is
available from the work of Clausius and Schachin-
ger,[29] and Rayne and Kemp.[30] Rayne and Kemp
have analyzed the data of Busey and Giauque[28] and
found the electronic-heat-capacity coefficient to
be 7.05 mJ/K^2 mol and the spin-wave contribution
to the heat capacities to be $8.8 \times 10^{-5} T^{3/2}$ J/K mol.
These workers have remarked that "owing to its
large electronic heat capacity, it is not possible
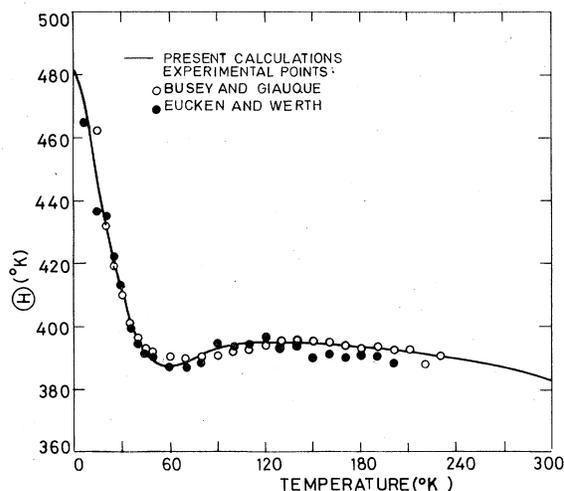to determine the value of Θ for nickel with any

great accuracy." Further, there is an attendant
uncertainty in the electronic heat capacity due to
the unknown impurity content of the specimens
used in measurements. We have subtracted here
the electronic and spin-wave contributions to the
specific heat from the recent measurements of
Rayne and Kemp. George and Thomson[31] have re-
cently reported the C_v data of nickel using a dif-
ferent technique. They have directly utilized the
experimental results on temperature-dependent
saturation magnetization. Their values for Θ are
in agreement with those obtained by Rayne and
Kemp for temperatures $T < 150$ K, but are signifi-
cantly higher than these values for $200 < T < 300$ K.

A perusal of Figs. 1–3 show that the present
phenomenological scheme, attributing the Cauchy
discrepancy to both angular (noncentral) and vol-
ume interactions, produces a reasonable picture
of the observed crystal dynamics of nickel and it
therefore justifies the adequacy of the present
formalism. In conclusion, we can say that the
present approach, while taking into account the
effect of the electron gas in a rather primitive
way, predicts reasonably well the dynamical pro-
perties of Ni indicating thereby that angular forces
play a significant role in the crystal dynamics of
Ni. The contribution of these noncentral forces is
estimated to be about 9% in magnitude as com-
pared to the total interactions taking place in the
ionic lattice of Ni. Though the present study is
confined to the lattice dynamics of Ni only, simi-
lar results are obtained for other fcc metals also.
As compared to complicated pseudopotential cal-
culations, the present phenomenological scheme
appears to be a convenient choice for the lattice-
dynamical description of nickel.

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