Anomalous lattice dynamics of ruthenium

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The lattice dynamics of the transition metal ruthenium is investigated both by inelastic neutron-scattering experiments and by *first-principles* density-functional perturbation calculations. There is excellent agreement between experiment and theory. We observe many phonon anomalies, in particular in the vicinity of the *M* point at the Brillouin-zone boundary, which are unique among the class of elements with hexagonal structure. Theoretical analysis provides evidence that they are not due to nesting effects but arise from a significant momentum dependence of the electron-phonon coupling matrix elements.

Transition metals have attracted continuous attention of both physicists and chemists because of their unusual electronic and structural properties, which have their origin in the dominant influence of *d* electrons on the electronic structure. They often exhibit pronounced phonon anomalies as a result of complex Fermi-surface geometries in conjunction with strong electron-phonon coupling (EPC), whose consistent description still provides a challenge for theoretical approaches. While a qualitative understanding could be achieved by semiphenomenological models,[1] methods based on density-functional theory possess the potential for a quantitative description without adjustable parameters. Among these *first-principles* schemes, the only attempt to establish a relationship between phonon anomalies and Fermi-surface properties has been undertaken for Rh using a supercell approach in combination with a simplified form for the EPC.[2] Applying a generalized supercell technique, the same type of anomaly as found in Rh has been successfully predicted for Ir.[3] Similar calculations for Ru provided evidence for very anomalous phonon branches, but failed in a reliable description of the phonon spectrum because of a very long-range of the lattice interactions.[4] In such a case, perturbative schemes[5] are more appropriate, which have already been applied to a variety of cubic transition metals.[6] While also properties of the EPC have been calculated within this framework, no attempt has yet been made to establish links to the observed phonon anomalies.

In this paper, we present a comprehensive experimental and theoretical investigation of the lattice dynamics of the hexagonal close-packed (hcp) transition-metal ruthenium. Phonon dispersion relations along all high-symmetry directions as well as for selected low-symmetry directions have been mapped out by inelastic neutron-scattering experiments. Theoretically, the phonon spectrum is calculated within density-functional perturbation theory in excellent agreement with the experimental results. The phonon spectrum exhibits various anomalies, in particular near the *M* point at the Brillouin-zone boundary. We elucidate its physical origin in a consistent way by analyzing the EPC within the same theoretical framework.

The neutron experiments were performed on a single crystal purchased from the Kristallhandel Kelpin Company. It had a volume of ≈ 1.5 cm^3 and a mosaic spread of less than 0.5°. The measurements were carried out on the 2T triple-axis spectrometer located at the Orphee reactor of the Laboratoire Léon Brillouin at Saclay. Cu(111) and pyrolytic graphite (002) crystals were used as monochromator and analyzer, respectively. The large size and the very good neutron-scattering properties of the sample allowed us to obtain high quality data in a rather short time. Error bars of the data shown in Fig. 1 are about the size of the symbols. These data were taken at room temperature. Selected phonons were investigated also as a function of temperature. These experiments revealed a hardening of phonon frequencies on cooling from $T = 295$ K to 12 K between 0.3 and 1.3%, on average by 0.7%. We note that selected phonon branches have been measured previously in an unpublished neutron-scattering investigation, whose results are mostly in good agreement with our data.[7]

Theoretical calculations are performed within a pseudopotential approach based on density-functional theory. The local-density approximation is applied using the Hedin-Lundqvist form of the exchange-correlation functional.[8] A norm-conserving pseudopotential for Ru was constructed according to a scheme proposed by Hamann-Schlüter-Chiang.[9] A mixed-basis set is employed to represent the valence states, consisting of five *d*-type local functions at each Ru site, smoothly cut off at a radius of 2.3 a.u., and of plane waves up to a kinetic energy of 22 Ry. For Brillouin-zone (BZ) integration we applied the special-point sampling technique in conjunction with Gaussian broadening of the energy levels of 0.2 eV. The phonon spectrum is calculated using density-functional perturbation theory,[5] which has been recently implemented for the mixed-basis method.[10] We found

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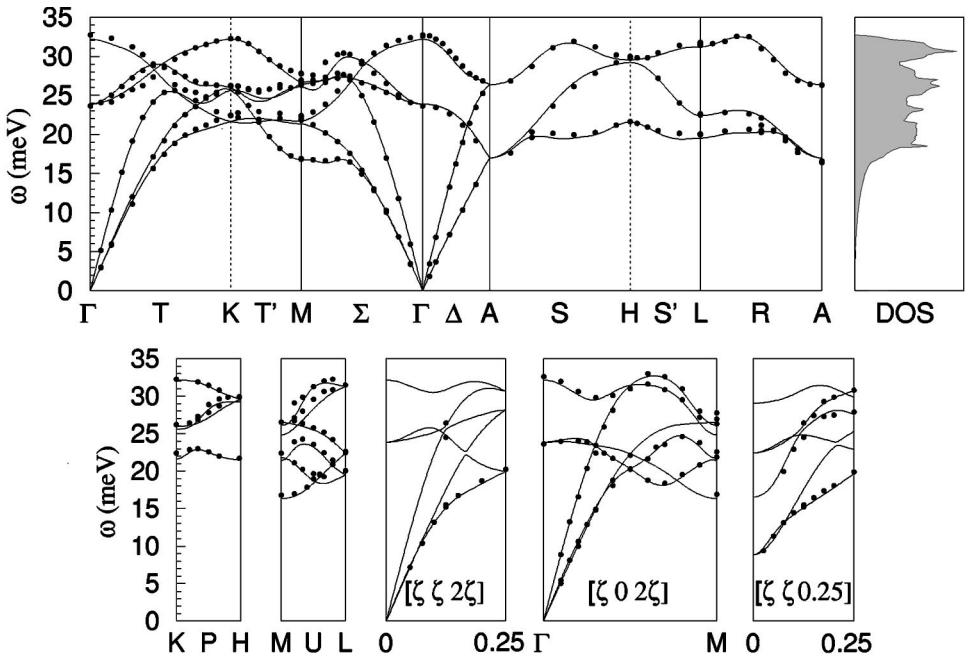

FIG. 1. Phonon dispersion curves of Ru for various directions in reciprocal space. Neutron-scattering data are given as dots, theoretical results as lines. The theoretical phonon density of states (DOS) is also shown.

that a relatively dense mesh of k points is needed to achieve convergence of phonon frequencies because the Fermi surface of Ru is very complex. We used a $18\times18\times12$ simple hexagonal k-point mesh corresponding to 222 special points in the irreducible wedge of the BZ, for which frequencies were converged better than 0.5 meV. Complete dispersion curves are calculated by Fourier interpolation[11,12] of the dynamical matrices obtained on a simple hexagonal $9\times9\times6$ mesh. For the high symmetry directions in the $q_z=0$ plane we have also performed linear interpolations using a mesh twice as dense in order to obtain a better resolution of the dispersion anomalies described below.

Table I shows results for the static equilibrium structure as obtained from minimizing the total energy. The bulk modulus is extracted from a fit of $E_{\min}(V)$, where V denotes the cell volume, to the Murnaghan equation of state, while keeping the ratio c/a at the optimized value. While in general c/a varies with V, test calculations have shown that this has a negligible influence on the bulk modulus, as found previously by Fast *et al.*[13] Our results show very good agreement with experimental data as well as with previous theoretical studies.[13–15]

Figure 1 gives a summary of experimental (dots) and theoretical (lines) dispersion curves for various high symmetry directions as well as for selected low-symmetry directions in the hexagonal BZ. There is obviously excellent agreement between data and calculated results. Our results for branches along [001] (Γ-A, parallel to the hexagonal axis) are in accord with an earlier neutron-scattering experiment[16] and exhibit the anomalous flattening of the longitudinal branch near the zone boundary. In addition, we observe pronounced anomalies in all branches in the vicinity of the M point ($\frac{1}{2}$ 0 0). Their fingerprints can be most clearly seen in the dispersion curves along [100] (Γ-M), shown in Fig. 2: (i) the longitudinal modes (Σ_1) exhibit a sudden drop in frequency when approaching the BZ boundary; (ii) the acoustic branch of the in-plane transverse vibrations (Σ_4) is essentially dispersionless for more than $\frac{1}{3}$ of the Γ-M distance; (iii) the z-polarized branches (Σ_3) are almost degenerate at M. These anomalous features have not been observed so far for other elementary hcp metals.[17]

The theoretical approach allows an analysis of the lattice interaction in real space by Fourier transformation of the dynamical matrices obtained on the reciprocal space mesh. The presence of phonon anomalies is reflected in a very slow decay of certain real-space force constants with increasing

TABLE I. Bulk properties of ruthenium. Experimental low-temperature structural data are taken from Ref. 23, and bulk modulus from Ref. 24.

	a(Å)	c(Å)	c/a	B (Mbar)	dB/dP
Mixed basis	2.701	4.270	1.580	3.28	4.3
Experiment	2.703	4.274	1.581	3.21	

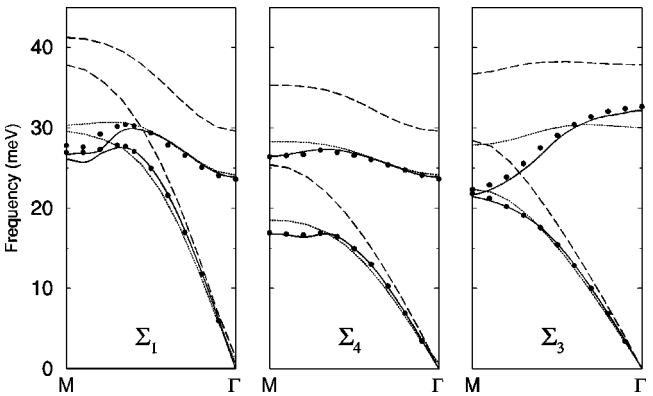

FIG. 2. Phonon dispersion curves of Ru along [100] for the three irreducible representations. Shown are theoretical branches obtained for the complete calculation (full lines), without $\Phi^{(EPC)}$ contributions from four bands crossing the Fermi level (dashed lines), and with an averaged value for the band-energy dependent factor of Eq. (1) (dotted lines). Black dots represent experimental data.

bond length. We find two types of long ranged couplings: (i) a slow decay of zz-polarized couplings along the zigzag chain of atoms parallel to the hexagonal axis, which are significant up to the sixth neighboring plane, and (ii) a long ranged interaction of predominantly longitudinal character along a chain of atoms containing the nearest-neighbor in-plane atom, extending at least to the third nearest neighbor. Because of this long ranged nature of the lattice interaction, an application of the generalized supercell technique to Ru was of limited accuracy[4] indicating that the present perturbative method is a more efficient approach to describe anomalous features of the phonon dispersion relations.

These conclusions are corroborated by attempts to describe the data by an empirical model using tensor forces for the nearest and next-nearest neighbors, and axially symmetric forces for more distant neighbors. We found that the model had to include forces up to the 20th neighbor with as many as 42 adjustable parameters to achieve a description about as good as obtained by the *ab initio* calculations. Even this model failed, however, to reproduce some fine-structure in the dispersion curves indicating that the effective force field extends beyond the 20th neighbor. The model calculations further revealed that information on the phonon intensities had to be included into the fit procedure to achieve a reliable description of the inelastic structure factors, a quantity which was also very well predicted by the *ab initio* calculations.

Phonon anomalies have been observed for most transition metals studied until now. While it is commonly believed that their origin lies in the coupling of lattice vibrations to electronic states near the Fermi energy, the question arises whether the Fermi geometry or the EPC matrix elements are more relevant. Early investigations on Pt and Pd[18] explained the appearance of anomalies as a Kohn effect,[19] which relies on a strong coupling to electronic transitions between two almost parallel sheets of the Fermi surface (FS), i.e., on a nesting condition. On the other hand, an analysis of phonon anomalies in Nb and Mo within a tight-binding approach emphasized the importance of the momentum dependence of EPC matrix elements.[1] The latter viewpoint is corroborated by a recent *ab initio* analysis of the phonon spectra of Rh using a simplified expression for the EPC matrix elements.[2]

The present perturbative approach allows a more detailed analysis of the M-point anomalies of Ru without further approximation. The starting point is an EPC related contribution to the force constant matrix, which can be written in the form

$$\Phi^{(EPC)}_{\kappa a \kappa' a'}(\mathbf{q}) = \frac{2}{N} \sum_{\nu\nu'} \sum_{\mathbf{k}} \frac{f_{\mathbf{k+q}\nu} - f_{\mathbf{k}\nu'}}{\epsilon_{\mathbf{k+q}\nu} - \epsilon_{\mathbf{k}\nu'}} g^{\kappa a *}_{\mathbf{k+q}\nu,\mathbf{k}\nu'} g^{\kappa' a'}_{\mathbf{k+q}\nu,\mathbf{k}\nu'} . \tag{1}$$

Here, $\epsilon_{\mathbf{k}\nu}$ denotes the energy of a Kohn-Sham orbital with momentum $\mathbf{k}$ and band index ν, $f_{\mathbf{k}\nu}$ its fractional occupation number, and N the number of unit cells, while the factor 2 is due to the spin degrees of freedom. $g^{\kappa a}$ is the matrix element describing the coupling of electronic states to a displacement of atom κ in the direction a. For the present mixed-basis scheme it is given by the first-order variation of the Kohn-Sham Hamiltonian $H_{\alpha\beta}$ and the overlap matrix $S_{\alpha\beta}$ as

$$g^{\kappa a}_{\mathbf{k+q}\nu,\mathbf{k}\nu'}(\mathbf{q}) = \sum_{\alpha\beta} c^*_\alpha(\mathbf{k+q}\nu) c_\beta(\mathbf{k}\nu') \times \left\{ \delta^{\mathbf{q}}_{\kappa a} H^{\mathbf{k}}_{\alpha\beta} - \frac{\epsilon_{\mathbf{k+q}\nu} + \epsilon_{\mathbf{k}\nu'}}{2} \delta^{\mathbf{q}}_{\kappa a} S^{\mathbf{k}}_{\alpha\beta} \right\}, \tag{2}$$

where $c_\alpha(\mathbf{k}\nu)$ are the expansion coefficients of the valence state $(\mathbf{k}\nu)$ with respect to the basis functions $|\chi_\alpha\rangle$ (for details see Ref. 10). The second term inside the bracket is a correction which arises from the nonorthogonality of the mixed-basis set, and appears also in other band-structure formalisms.[1,6] A term similar to $\Phi^{(EPC)}$ is also present in the tight-binding description of the dynamical matrix (called D_2 in Ref. 1) and has been found to incorporate the main contribution to the phonon anomalies observed in Nb and Mo.

The FS of Ru has a rather complex geometry. Four valence bands cross the Fermi energy giving rise to six separate surfaces. The present nonrelativistic calculation provides a good description of the FS geometry, as inferred from the close similarity of our Kohn-Sham band structure to those of the relativistic linear muffin-tin orbital calculation of Jepsen, Andersen, and Mackintosh,[20] with the exception of a slight broadening of the overall valence bandwidth of $\approx 5\%$. According to Eq. (1), we have calculated the contribution to $\Phi^{(EPC)}$ arising from scattering processes among these four bands, which is then *subtracted* from the total force constants. The resulting dispersion curves along [100] are plotted as dashed lines in Fig. 2. They exhibit a normal behavior, indicating that the anomalous features are indeed linked to the four bands crossing the Fermi level. A closer inspection shows that the anomalous q dependence cannot be attributed to a single FS sheet or band alone, but all scattering processes $\nu \rightarrow \nu'$ among these four bands contribute comparably, with a slight preference for interband processes. It is also not due to a nesting property of the FS, which would result in a pronounced q dependence of the band-energy dependent factor in Eq. (1). To demonstrate this, we have performed an approximate calculation of $\Phi^{(EPC)}$ by using a $\mathbf{k}$- and $\mathbf{q}$-averaged value of this factor for the contribution of the four FS bands. The resulting phonon dispersions, shown as dotted lines in Fig. 2, still exhibit the anomalous features discussed above, albeit less pronounced, which indicates that the q dependence of the EPC matrix elements is of primary importance for the observed anomalies.

In summary, we have performed a comprehensive investigation of the lattice dynamics of the hcp metal Ru using both inelastic neutron-scattering experiments and first-principles calculations. We found an excellent agreement between experimental and theoretical dispersion curves. Anomalies were detected in various phonon branches, most pronounced in the vicinity of the M point. A theoretical analysis confirmed that the anomalies arise from a strong coupling of lattice vibrations to electronic transitions among the four bands crossing the Fermi level, and stressed the importance of the momentum dependence of the EPC matrix elements. This demonstrates that the present computational method is a powerful tool to very accurately predict phonon spectra even in the presence of complex phonon anomalies, and to provide at the same time a consistent picture of its physical origin.

The phonon anomalies of Ru constitute an additional type of anomalies among the class of hcp elemental metals studied so far. In view of the similar electronic structure and FS geometry, osmium is another candidate which may exhibit this type of anomalies. The present findings should be further of relevance for a proper analysis and interpretation of phonon measurements on clean and adsorbate covered Ru surfaces.[21,22]

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