

Frequencies and polarization vectors of phonons: Results from force constants which are fitted to experimental data or calculated *ab initio*

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The properties of phonons may be calculated from the dynamical matrix which is determined by force constants. Often the force constants are obtained by fitting them to experimental phonon frequencies, e.g., for wave vectors \mathbf{q} on high-symmetry directions of the Brillouin zone. It is well known that these force constants do not necessarily lead to correct frequencies for wave vectors for nonsymmetrical \mathbf{q} and to correct polarization vectors. In the present paper this is demonstrated by comparing for fcc Ni, fcc Al, and bcc Fe the frequencies and polarization vectors calculated from fitted force constants with the results from *ab initio* calculated force constants. However, for most regions of the Brillouin zone the differences between the results obtained from the two sets of force constants are not large.

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I. INTRODUCTION

In the theory of lattice dynamics the force-constant matrix plays an important role. For a solid with an elementary unit cell containing just one atom of mass M the elements of the force-constant matrix $\underline{\phi}(\mathbf{T}, \mathbf{T}')$ between the atoms in the elementary unit cells at the translation vectors \mathbf{T} and \mathbf{T}' are

$$\phi_{nm}(\mathbf{T}, \mathbf{T}') = - \left. \frac{\partial F_m(\mathbf{T}')}{\partial u_n(\mathbf{T})} \right|_{u_n=0} = - \lim_{u_n \rightarrow 0} \frac{F_m(\mathbf{T}')}{u_n(\mathbf{T})}. \quad (1)$$

Here n and m denote the three Cartesian directions x , y , and z , $u_n(\mathbf{T})$ is the n component of a small displacement $\mathbf{u}(\mathbf{T})$ of the atom in the unit cell at \mathbf{T} and $F_m(\mathbf{T}')$ is the m component of the force on the atom at \mathbf{T}' resulting from this displacement. For a general situation with small displacements $\mathbf{u}(\mathbf{T}')$ of the atoms in the cells with translation vector \mathbf{T}' , Newton's equations of motion for the displacements read

$$M \frac{\partial^2 \mathbf{u}(\mathbf{T})}{\partial t^2} = - \sum_{\mathbf{T}'} \underline{\phi}(\mathbf{T}, \mathbf{T}') \mathbf{u}(\mathbf{T}'). \quad (2)$$

The solutions of Eq. (2) are plane waves with displacements

$$\mathbf{u}(\mathbf{T}, t) = \frac{u_0}{\sqrt{M}} \mathbf{e}(\mathbf{q}) \exp\{i[\mathbf{q} \cdot \mathbf{T} - \omega(\mathbf{q})t]\}, \quad (3)$$

where $\mathbf{e}(\mathbf{q})$ and u_0 denote the direction and the amplitude of the displacement for the phonon mode with wave vector \mathbf{q} . Inserting Eq. (3) into Eq. (2) yields

$$\underline{\underline{D}}(\mathbf{q}) \mathbf{e}(\mathbf{q}) = \omega^2(\mathbf{q}) \mathbf{e}(\mathbf{q}). \quad (4)$$

Here $\underline{\underline{D}}(\mathbf{q})$ is the dynamical matrix

$$\underline{\underline{D}}(\mathbf{q}) = \frac{1}{M} \sum_{\mathbf{T}'} \underline{\phi}(0, \mathbf{T}') \exp(i\mathbf{q}\mathbf{T}'). \quad (5)$$

$\underline{\underline{D}}(\mathbf{q})$ is a symmetric 3×3 matrix, and thus the eigenvalue equation (4) yields for each \mathbf{q} three eigenvectors $\mathbf{e}_j(\mathbf{q})$ and three eigenvalues $\omega_j^2(\mathbf{q})$, $j = 1, 2, 3$, which depend on $\underline{\phi}(0, \mathbf{T}')$,

$$\omega_j^2(\mathbf{q}) = \omega_j^2(\mathbf{q}; \{\underline{\phi}(0, \mathbf{T}')\}). \quad (6)$$

If these vibronic eigenmodes are quantized, then they are called phonons.

The $\omega_j^2(\mathbf{q})$ can be directly determined by neutron spectroscopy. The force constants then are usually determined by fitting the theoretical $\omega_j^2(\mathbf{q}; \{\underline{\phi}(0, \mathbf{T}')\})$ to the measured frequencies for wave vectors \mathbf{q} on high-symmetry directions of the phonon Brillouin zone (see Refs. 1 and 2 for Ni) or to the phonon density of states (see Ref. 3 for Ni). However, Foreman and Lomer⁴ as well as Leigh *et al.*⁵ have shown that the force constants cannot be deduced from the lattice frequencies alone. The fact that a set of force constants gives nearly exact frequencies does not mean that the force constants are correct. Leigh *et al.*⁵ showed that application of a unitary transformation to any set of $\underline{\phi}(0, \mathbf{T}')$ may alter individual force constants while leaving the frequencies unchanged. Thereby the unitary transformation is not arbitrary but it must fulfill several requirements, e.g., the transformed $\underline{\phi}(0, \mathbf{T}')$ must also exhibit the correct symmetry of the lattice. Altogether, an infinite number of sets of force constants give the same frequencies but distinct eigenvectors $\mathbf{e}(\mathbf{q})$. These findings have been illustrated by numerical examples in Refs. 5 and 6. This ambiguity can be resolved only⁴⁻⁶ when the eigenvectors are also known. The eigenvectors enter differential cross sections for the neutron scattering, but the measurement of just the cross sections does not generally suffice to determine the eigenvectors unambiguously. Kohl has shown⁷ that orienting the crystal near a Bragg position in coherent inelastic neutron scattering yields additional information on the eigenvectors which can be used to get unambiguous values for the force constants. This formalism has been applied to Si (Ref. 8) and to Si as well as GaAs in Ref. 9.

Suppose that a set of force constants has been obtained by a fit to the experimental phonon frequencies for wave vectors \mathbf{q} on high-symmetry directions of the Brillouin zone, which yields a very good agreement of the theoretically calculated frequencies and the experimental frequencies. Because of the above-discussed ambiguity it is not guaranteed that this set yields accurate frequencies also for nonsymmetrical \mathbf{q} .

Furthermore, it is not guaranteed that the set yields good eigenvectors, even for wave vectors along the high-symmetry directions for which the force constants have been fitted to the experimental frequencies. In the literature there are indeed only a few papers which consider the eigenvectors, i.e., the polarization vectors $\mathbf{e}_j(\mathbf{q})$. However, the knowledge of these eigenvectors is important in several contexts. For instance, a matrix element for the scattering of an electron at a phonon with wave vector \mathbf{q} and eigenvector $\mathbf{e}_j(\mathbf{q})$ contains¹⁰ this $\mathbf{e}_j(\mathbf{q})$. Furthermore, the $\mathbf{e}_j(\mathbf{q})$ are important for a discussion of phonon states which carry an angular momentum. A phonon eigenstate with polarization vector $\mathbf{e}_j(\mathbf{q})$ does not carry a sharp angular momentum, and the corresponding expectation value of angular momentum is zero. Only for special wave vectors are the phonon eigenstates $\mathbf{e}_j(\mathbf{q})$ degenerate, i.e., they have the same $\omega_j^2(\mathbf{q})$ for different j , and these degenerate states can be combined to stationary states with circular or elliptical polarizations possessing angular momentum. Of course it is possible to also form arbitrarily many coherent superpositions of other phonon eigenstates, superpositions which do not represent stationary states but which have nonzero expectation values of angular momentum. These considerations are important for the discussion of the damping of the magnetization dynamics, because thereby angular momentum is transferred from the spin system to the crystal via electron-phonon scattering.^{10,11} Recently, angular-momentum transfer in electron-phonon scattering has been observed experimentally¹² by resonant inelastic x-ray scattering.

Instead of trying to determine the force constants from experimental data, they can be calculated by phenomenological models or by *ab initio* calculations. It thereby turned out¹³ that the eigenvectors calculated from the force constants by use of the various models may differ markedly among each other and from the *ab initio* calculated eigenvectors, although all of them reproduce the experimental phonon frequencies very closely. Clearly, well-converged *ab initio* calculations are more reliable than calculations based on phenomenological models.

In the present paper the force constants of fcc Ni, fcc Al, and bcc Fe are calculated by use of the *ab initio* spin-density-functional electron theory. The scope of our paper is not to demonstrate that phonon dynamics can be very successfully investigated by present-day applications of robust *ab initio* methods. This has been already demonstrated in many papers (for a review, see Ref. 14), not just for elementary materials (see Ref. 15 for Fe and Ni) or metallic compounds¹⁶ but also for complicated systems like high- T_c superconductors (see, e.g., Ref. 17) or negative-thermal-expansion materials (see, e.g., Ref. 18). The main scope is to investigate how strongly the polarization vectors obtained from force constants fitted to experimental phonon data differ from the polarization vectors calculated from force constants determined *ab initio*.

II. CALCULATIONAL PROCEDURE

In our *ab initio* calculations of the force constants, the direct approach¹⁹ is used (which is an alternative to the linear response approach²⁰). There are two versions of the direct approach, a frozen-phonon calculation and the direct force-constant approach. In this latter approach, which is used in the present paper, single atoms in the crystal are displaced,

the resulting forces are calculated *ab initio*, and the force constants are determined via Eq. (1). Thereby, instead of displacing a single atom in an infinitely extended system, a supercell containing many elementary unit cells is constructed and a single atom within the supercell is displaced. Because the supercells then are repeated periodically with the translation vectors \mathbf{T}^{sc} , there is a periodic array of displaced atoms, and the force on a considered atom is given by a superposition of the forces exerted by all the displaced atoms on the considered atom. Therefore the supercell calculations do not yield the true force constants, but effective force constants. Nevertheless, when calculating from these effective force constants the dynamical matrix $\underline{D}(\mathbf{q})$ according to Eq. (5), the exact dynamical matrix and hence the exact frequencies and eigenvectors are obtained for wave vectors \mathbf{q} which correspond to vectors of the reciprocal lattice of the supercell lattice, i.e., if $\mathbf{q} \cdot \mathbf{T}^{\text{sc}} = 2\pi n$, $n \in \mathbb{Z}$; see Ref. 16. It is expected that for general wave vectors the results represent a good interpolation between these exact data, and this has been confirmed for B2-FeAl in Ref. 16.

The calculations were performed with the PWSCF code,²¹ using Vanderbilt ultrasoft pseudopotentials²² and the generalized gradient approximation.²³ For Fe the 3s and 3p states are treated as true core states, and for Ni as semicore states. We used the experimental lattice constants a_0 at zero temperature, 4.032 Å for Al, 2.860 Å for Fe, and 3.5155 Å for Ni. Having performed the respective convergence tests, the plane-wave cutoff was set to 25 Ry for Al and 30 Ry for Fe and Ni. The cutoff for the representation of the electron density was 120 Ry for Al and 200 Ry for Fe and Ni. For the k -point-sampling k -point nets equivalent to a certain Monkhorst-Pack mesh²⁴ in the Brillouin zone of the respective conventional unit cell were used, the mesh being $(24 \times 24 \times 24)$ for Al, $(20 \times 20 \times 20)$ for Fe, and $(12 \times 12 \times 12)$ for Ni, and a Gaussian smearing with width 0.136 eV was used for all three materials. Supercells of different sizes were considered; we give the results for the largest supercell for each material, $(4 \times 4 \times 4)$ for Al, $(4 \times 4 \times 4)$ for Ni, $(5 \times 5 \times 5)$ for Fe, all as multiples of the conventional unit cells (with orthogonal translation vectors). Due to the symmetry it suffices to displace the central atom along one positive Cartesian direction n by the amplitudes $u_n(0)$ to get all force constants from the forces $F_m(\mathbf{T}')$ according to Eq. (1). The calculations were performed for $u_n(0) = (0.1 \text{ \AA}) \times p$ with $p = 1, 2, \dots, 6$. A third-order polynomial was fitted to the data points for $F_m(\mathbf{T}')/u_n(0)$, and the force constants were calculated from the derivative of this polynomial at $u_n(0) = 0$.

III. RESULTS

In Tables I–III we compare for fcc Ni, fcc Al, and bcc Fe the force constants obtained by our *ab initio* calculations (for $T = 0$ K) with the force constants fitted by Kresch *et al.*^{3,25} and by Kresch²⁶ to the phonon density of states measured at $T = 10$ K for fcc Ni and fcc Al, and $T = 21$ K for bcc Fe. The numerical uncertainty of the *ab initio* force constants is about ± 0.03 N/m for Ni and Fe and ± 0.02 N/m for Al. Note that the *ab initio* force constants beyond the interaction ranges considered in the fits to experimental data are not vanishingly small.

TABLE I. Force constants (FCs) for fcc Ni in N/m from our *ab initio* calculations up to the 28th nearest neighbor (numerical uncertainty about ± 0.03 N/m) and force constants fitted to the experimentally determined phonon density of states at $T = 10$ K of Kresch *et al.* (Ref. 3) up to the 5th nearest neighbor. The neighbor position (NP) is given in units of $a_0/2$. The force constants $\phi_{i, nm}$ of the force-constant matrix $\phi(0, T')$, entering Eq. (5), are labeled with the index of the i th nearest neighbor and with the Cartesian directions n and m . Note that the 15th, 16th, 19th, and 21st up to the 27th neighbors are outside the $(4 \times 4 \times 4)$ supercell.

NP	FC	<i>Ab initio</i>	Fit (Ref. 3)	NP	FC	<i>Ab initio</i>	NP	FC	<i>Ab initio</i>	NP	FC	<i>Ab initio</i>
(1,1,0)	$\phi_{1,xx}$	17.02	17.584	(2,2,2)	$\phi_{6,xx}$	0.02	(4,2,0)	$\phi_{11,xx}$	-0.02	(4,4,0)	$\phi_{17,xx}$	0.15
	$\phi_{1,zz}$	-0.23	-0.391		$\phi_{6,xy}$	0.07		$\phi_{11,yy}$	0.08		$\phi_{17,zz}$	0.04
	$\phi_{1,xy}$	19.05	18.976	(3,2,1)	$\phi_{7,xx}$	-0.16		$\phi_{11,zz}$	0.00	$\phi_{17,xy}$	0.00	
(2,0,0)	$\phi_{2,xx}$	2.05	0.975		$\phi_{7,yy}$	0.04	(2,3,3)	$\phi_{11,xy}$	0.00	(4,3,3)	$\phi_{18,xx}$	-0.02
	$\phi_{2,yy}$	-0.87	-0.610	$\phi_{7,zz}$	-0.01	$\phi_{12,xx}$		0.03	$\phi_{18,yy}$		-0.01	
(2,1,1)	$\phi_{3,xx}$	1.22	0.593	(4,0,0)	$\phi_{7,xy}$	-0.01	(4,2,2)	$\phi_{12,yy}$	-0.02	(2,4,4)	$\phi_{18,xy}$	0.00
	$\phi_{3,yy}$	0.44	0.302		$\phi_{7,xz}$	-0.14		$\phi_{12,xy}$	0.02		$\phi_{18,yz}$	0.01
	$\phi_{3,xy}$	0.75	0.378		$\phi_{7,yz}$	-0.12		$\phi_{12,yz}$	0.03		$\phi_{20,xx}$	0.00
(2,2,0)	$\phi_{3,yz}$	0.04	-0.120	(3,3,0)	$\phi_{8,xx}$	-0.09	(4,3,1)	$\phi_{13,xx}$	0.05	(4,4,4)	$\phi_{20,yy}$	0.00
	$\phi_{4,xx}$	0.13	0.386		$\phi_{8,yy}$	-0.05		$\phi_{13,yy}$	-0.02		$\phi_{20,xy}$	0.00
	$\phi_{4,zz}$	-0.15	-0.218	$\phi_{9,xx}$	0.42	$\phi_{13,xy}$		0.00	$\phi_{20,yz}$		0.00	
(3,1,0)	$\phi_{4,xy}$	0.15	0.517	(4,1,1)	$\phi_{9,zz}$	-0.02	(4,3,1)	$\phi_{13,yz}$	0.04		$\phi_{28,xx}$	0.00
	$\phi_{5,xx}$	-0.03	-0.085		$\phi_{9,xy}$	0.40		$\phi_{14,xx}$	-0.07		$\phi_{28,xy}$	0.00
	$\phi_{5,yy}$	-0.03	0.006	$\phi_{10,xx}$	-0.01	$\phi_{14,yy}$		-0.04				
	$\phi_{5,zz}$	-0.12	0.014	$\phi_{10,yy}$	0.04	$\phi_{14,zz}$		0.00				
	$\phi_{5,xy}$	-0.07	-0.039	$\phi_{10,xy}$	0.00	$\phi_{14,xy}$		0.00				
				$\phi_{10,yz}$	-0.04	$\phi_{14,xz}$	0.00					
						$\phi_{14,yz}$	-0.04					

It becomes obvious that the force constants which were obtained from a fit to the experimental phonon density of states deviate from the *ab initio* force constants. The deviations are slightly larger for Al and Fe than for Ni. Thereby the deviations are clearly visible but they are not “arbitrarily” large. This probably results from the fact that the unitary transformations which may be applied to a force-constant matrix without changing the frequencies are not arbitrary but

must fulfill several requirements (see the Introduction). It is the most important finding of our investigations that the fitted coupling constants are rather close to the “true” force constants obtained from *ab initio* calculations.

In the next step of our investigations we want to figure out the quantitative effect of the differences between these two sets of force constants on the frequencies and on the polarization vectors of the phonons. In Figs. 1(a), 2(a), and 3(a) we compare

TABLE II. Force constants for fcc Al in N/m from our *ab initio* calculations up to the 28th nearest neighbor (numerical uncertainty about ± 0.02 N/m) and force constants fitted to the experimentally determined phonon density of states at $T = 10$ K of Kresch *et al.* (Ref. 25) up to the eighth nearest neighbor. The notation is the same as in Table I.

NP	FC	<i>Ab initio</i>	Fit (Ref. 25)	NP	FC	<i>Ab initio</i>	Fit (Ref. 25)	NP	FC	<i>Ab initio</i>	NP	FC	<i>Ab initio</i>
(1,1,0)	$\phi_{1,xx}$	10.62	10.112	(2,2,2)	$\phi_{6,xx}$	-0.11	0.144	(4,2,0)	$\phi_{11,xx}$	-0.06	(4,4,0)	$\phi_{17,xx}$	0.02
	$\phi_{1,zz}$	-1.81	-1.356		$\phi_{6,xy}$	-0.18	-0.110		$\phi_{11,yy}$	0.03		$\phi_{17,zz}$	-0.02
	$\phi_{1,xy}$	11.26	11.148	(3,2,1)	$\phi_{7,xx}$	0.07	-0.061		$\phi_{11,zz}$	0.01	$\phi_{17,xy}$	0.00	
(2,0,0)	$\phi_{2,xx}$	1.94	2.454		$\phi_{7,yy}$	0.03	-0.088	(2,3,3)	$\phi_{11,xy}$	0.00	(4,3,3)	$\phi_{18,xx}$	0.02
	$\phi_{2,yy}$	-0.03	-0.532	$\phi_{7,zz}$	-0.02	-0.105	$\phi_{12,xx}$		0.07	$\phi_{18,yy}$		-0.02	
(2,1,1)	$\phi_{3,xx}$	-0.40	-0.634	(4,0,0)	$\phi_{7,xy}$	0.05	0.032	(4,2,2)	$\phi_{12,yy}$	0.03	(2,4,4)	$\phi_{18,xy}$	0.00
	$\phi_{3,yy}$	-0.09	-0.298		$\phi_{7,xz}$	0.06	0.016		$\phi_{12,xy}$	0.03		$\phi_{18,yz}$	0.02
	$\phi_{3,xy}$	-0.30	-0.185		$\phi_{7,yz}$	0.01	0.011		$\phi_{12,yz}$	0.05		$\phi_{20,xx}$	-0.03
(2,2,0)	$\phi_{3,yz}$	-0.08	-0.149	(3,3,0)	$\phi_{8,xx}$	0.14	-0.536	(4,3,1)	$\phi_{13,xx}$	0.04	(4,4,4)	$\phi_{20,yy}$	-0.03
	$\phi_{4,xx}$	0.19	0.273		$\phi_{8,yy}$	-0.03	-0.117		$\phi_{13,yy}$	0.01		$\phi_{20,xy}$	0.00
	$\phi_{4,zz}$	-0.01	0.324	$\phi_{9,xx}$	-0.06	-0.01	$\phi_{13,xy}$		0.00	$\phi_{20,yz}$		0.00	
(3,1,0)	$\phi_{4,xy}$	0.31	-0.051	(4,1,1)	$\phi_{9,zz}$	-0.01	-0.05	(4,3,1)	$\phi_{13,yz}$	0.01		$\phi_{28,xx}$	-0.02
	$\phi_{5,xx}$	0.21	0.469		$\phi_{9,xy}$	-0.05	-0.05		$\phi_{14,xx}$	-0.04		$\phi_{28,xy}$	0.00
	$\phi_{5,yy}$	0.02	0.229	$\phi_{10,xx}$	-0.14	-0.14	$\phi_{14,yy}$		-0.03				
	$\phi_{5,zz}$	0.01	0.199	$\phi_{10,yy}$	-0.01	-0.01	$\phi_{14,zz}$		0.01				
	$\phi_{5,xy}$	-0.03	0.090	$\phi_{10,xy}$	0.00	0.00	$\phi_{14,xy}$		0.00				
				$\phi_{10,yz}$	0.01	0.01	$\phi_{14,xz}$	0.00					
							$\phi_{14,yz}$	-0.02					

TABLE III. Force constants for bcc Fe in N/m from our *ab initio* calculations up to the 32nd nearest neighbor (numerical uncertainty about ± 0.03 N/m) and force constants fitted to the experimentally determined phonon density of states at $T = 21$ K by Kresch (Ref. 26) up to the fifth nearest neighbor. Note that the 15th, 16th, 18th, 21st, 22nd, 23rd, and 25th up to the 31st neighbors are outside the $(5 \times 5 \times 5)$ supercell. The notation is the same as in Table I.

NP	FC	<i>Ab initio</i>	Fit (Ref. 26)	NP	FC	<i>Ab initio</i>	NP	FC	<i>Ab initio</i>	NP	FC	<i>Ab initio</i>
(1,1,1)	$\phi_{1,xx}$	15.79	17.263	(1,3,3)	$\phi_{7,xx}$	0.04	(5,1,1)	$\phi_{11,xx}$	-0.12	(5,3,3)	$\phi_{17,xx}$	0.19
	$\phi_{1,xy}$	12.32	14.910		$\phi_{7,yy}$	-0.21		$\phi_{11,yy}$	0.09		$\phi_{17,yy}$	-0.07
(2,0,0)	$\phi_{2,xx}$	15.29	15.314	$\phi_{7,xy}$	-0.01	$\phi_{11,xy}$	0.00	$\phi_{17,xy}$	0.00			
	$\phi_{2,yy}$	-0.10	0.115	$\phi_{7,yz}$	-0.09	$\phi_{11,yz}$	0.06	$\phi_{17,yz}$	-0.05			
(2,2,0)	$\phi_{3,xx}$	1.24	1.020	(4,2,0)	$\phi_{8,xx}$	-0.21	(4,4,0)	$\phi_{12,xx}$	0.17	(4,4,4)	$\phi_{19,xx}$	-0.17
	$\phi_{3,zz}$	-0.84	-0.393		$\phi_{8,yy}$	-0.17		$\phi_{12,zz}$	0.13		$\phi_{19,xy}$	0.03
	$\phi_{3,xy}$	0.60	0.273		$\phi_{8,zz}$	0.00		$\phi_{12,xy}$	0.06		(1,5,5)	$\phi_{20,xx}$
(3,1,1)	$\phi_{4,xx}$	0.57	-0.286	(4,2,2)	$\phi_{8,xy}$	-0.23	(5,3,1)	$\phi_{13,xx}$	0.00	$\phi_{20,yy}$		-0.03
	$\phi_{4,yy}$	0.39	0.048		$\phi_{9,xx}$	-0.41		$\phi_{13,yy}$	-0.01	$\phi_{20,xy}$	0.00	
	$\phi_{4,xy}$	0.54	-0.067		$\phi_{9,yy}$	-0.23		$\phi_{13,zz}$	0.02	$\phi_{20,yz}$	0.00	
	$\phi_{4,yz}$	0.47	0.566		$\phi_{9,xy}$	-0.19		$\phi_{13,xy}$	0.00	(3,5,5)	$\phi_{24,xx}$	0.01
(2,2,2)	$\phi_{5,xx}$	-0.82	-0.382	$\phi_{9,yz}$	-0.12	$\phi_{13,xz}$	0.00	$\phi_{24,yy}$	0.00			
	$\phi_{5,xy}$	-0.25	0.090	(3,3,3)	$\phi_{10,xx}$	-0.03	$\phi_{13,yz}$	-0.01	$\phi_{24,xy}$	0.00		
(4,0,0)	$\phi_{6,xx}$	0.44			$\phi_{10,xy}$	-0.20	(2,4,4)	$\phi_{14,xx}$	-0.01	$\phi_{24,yz}$	0.00	
	$\phi_{6,yy}$	0.09				$\phi_{14,yy}$		0.09	(5,5,5)	$\phi_{32,xx}$	0.10	
						$\phi_{14,xy}$		0.04		$\phi_{32,xy}$	0.00	
							$\phi_{14,yz}$	0.08				

for fcc Ni, fcc Al, and bcc Fe the frequencies for general wave vectors on a $(100 \times 100 \times 100)$ grid in the first octant of the first phonon Brillouin zone obtained from fitted force constants (ω_{fit}) and from *ab initio* force constants ($\omega_{\text{ab initio}}$). Shown are the relative differences $|\omega_{\text{fit}} - \omega_{\text{ab initio}}|/\omega_{\text{max}}$, where ω_{max} is the maximum frequency in the Brillouin zone (which is nearly the same for the two data sets). For most regions of the Brillouin zone the deviations between the two results are rather

small, smaller than 2.5% for Ni, smaller than 4.5% for Al, and smaller than 7% for Fe. There are small regions with deviations up to 2.9% for Ni, up to 5.2% for Al, and up to 9% for Fe.

To compare the results for the polarization vectors, we calculated for each \mathbf{q} the modulus of the scalar product between the polarization vectors obtained from the two sets of force constants. If this quantity is close to 1 then the corresponding polarization vectors are nearly parallel. Thereby we have

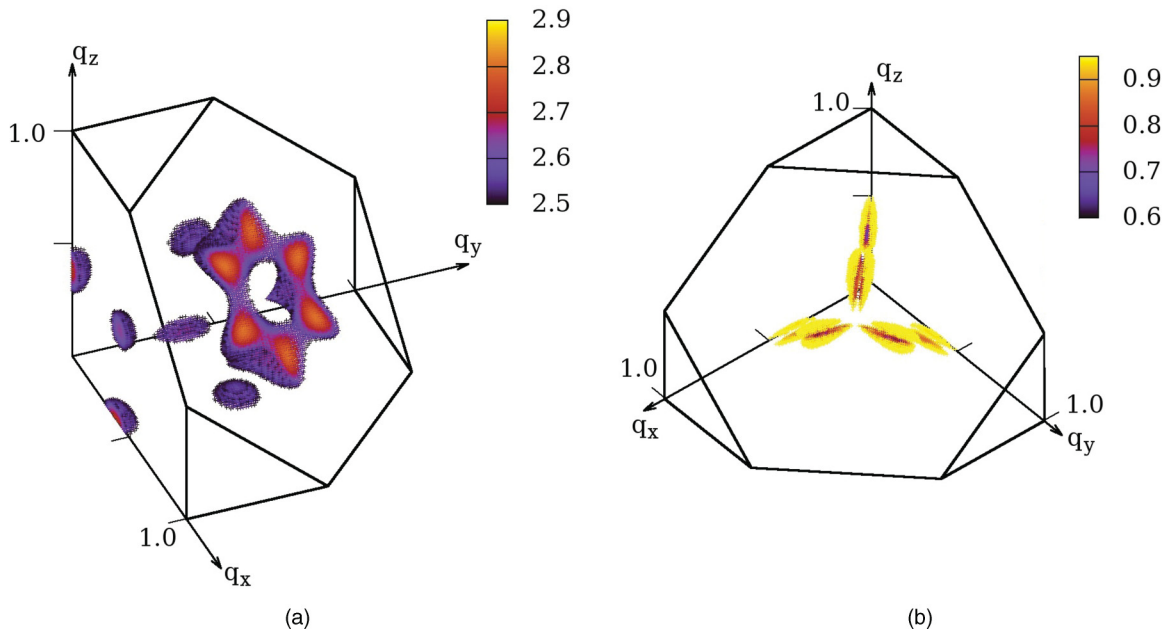


FIG. 1. (Color) Differences between the calculation with *ab initio* force constants and the calculation with fitted force constants (Ref. 3) for fcc Ni. In order to improve the readability only data for $q_x, q_y, q_z \geq 0$ (in units of $2\pi/a_0$) in the first phonon Brillouin zone are shown. (a) Relative phonon frequency deviation as a percentage (only greater than 2.5%); (b) modulus of the scalar product between the polarization vectors (only less than 0.95).

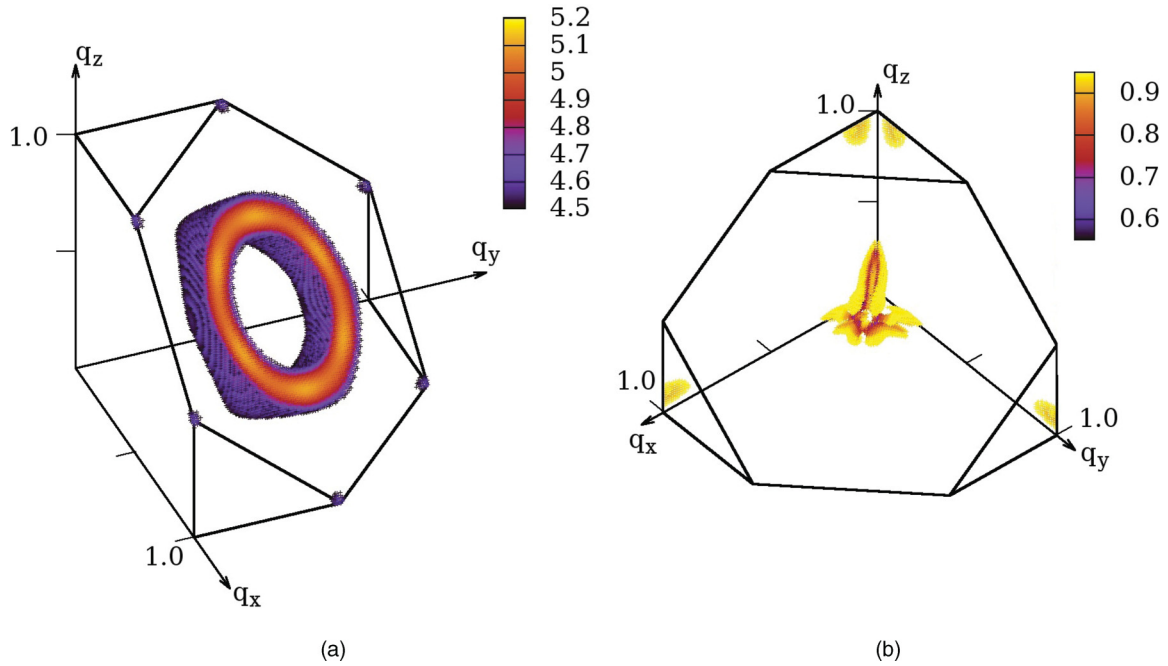


FIG. 2. (Color) Differences between the calculation with *ab initio* force constants and the calculation with fitted force constants (Ref. 25) for fcc Al. In order to improve the readability only data for $q_x, q_y, q_z \geq 0$ (in units of $2\pi/a_0$) in the first phonon Brillouin zone are shown. (a) Relative phonon frequency deviation as a percentage (only greater than 4.5%); (b) modulus of the scalar product between the polarization vectors (only less than 0.95).

omitted \mathbf{q} points where the frequencies of two approaching phonon branches are very close to each other, because at a real degeneracy point any arbitrary linear combination of phonon eigenvectors is again a phonon eigenvector. From Figs. 1(b), 2(b), and 3(b) it becomes obvious that there are only small

regions of the Brillouin zone for which the scalar products are smaller than 0.95 (down to about 0.6) for Ni and Al, and smaller than 0.995 (down to 0.98) for Fe. Obviously for Fe the differences between polarization vectors obtained from the two sets of force constants are smaller than for Ni and Al, although

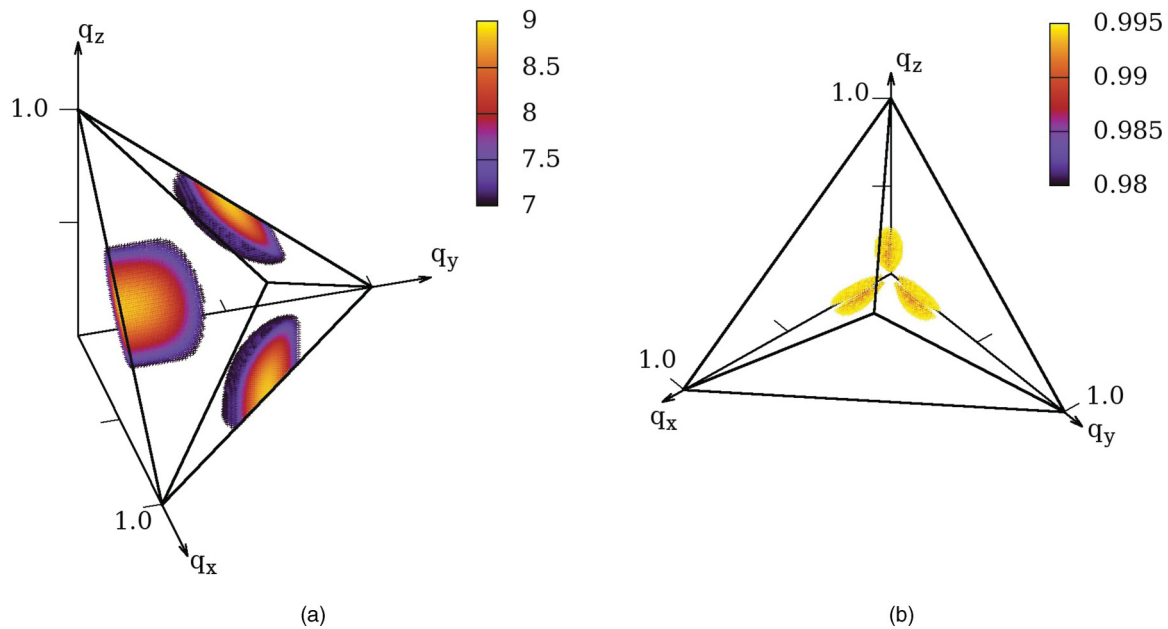


FIG. 3. (Color) Differences between the calculation with *ab initio* force constants and the calculation with fitted force constants (Ref. 26) for bcc Fe. In order to improve the readability only data for $q_x, q_y, q_z \geq 0$ (in units of $2\pi/a_0$) in the first phonon Brillouin zone are shown. (a) Relative phonon frequency deviation as a percentage (only greater than 7%); (b) modulus of the scalar product between the polarization vectors (only less than 0.995).

the differences between the two sets of force constants are larger.

IV. CONCLUSIONS

The meaning of force constants determined by fits to experimental phonon frequencies (or phonon density of states) is not really clear. The reason is that the application of a unitary transformation to any set of force constants alters individual force constants while leaving the frequencies (but of course not the polarization vectors) unchanged. The unitary transformation thereby must fulfill requirements, e.g., the transformed force-constant matrix must also exhibit the correct symmetry of the lattice. So far it was not clear how strongly these requirements reduce the differences between possible sets of force constants for which the experimental phonon data are fitted well. Therefore it was not clear how strongly the polarization vectors obtained from various of these sets of force constants differ from each other. In the present paper

we have investigated these questions by comparing fitted force constants with the “true” force constants from *ab initio* calculations. The investigations have been performed for fcc Ni, fcc Al, and bcc Fe, and we hope that the results are representative for other fcc and bcc metals and possibly for all three-dimensional metals. In our calculations the differences between the two sets of force constants are not large, and therefore the differences between the corresponding results for the frequencies and for the polarization vectors also are not large; they are rather small for most regions of the phonon Brillouin zone.

These findings have an important consequence for practical applications. If information on phonon polarization vectors is required, it is possible to obtain them from force constants fitted to experimental phonon frequencies. For three-dimensional metals it is very likely that these fitted force constants yield reliable polarization vectors, so that it is not necessary to calculate in each case the force constants and hence the polarization vectors *ab initio*.

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