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Abstract. The computational scheme of MacGillivray and Sholl for the calculation of the lattice Green's function is extended to crystalline compounds with more than one atom in the unit cell. The lattice Green's function is calculated for the high-temperature γ-phase of Fe and for the intermetallic compound FeTi using force constants obtained from Born–von Kármán fits to experimental lattice vibration spectra.

The properties of defects in crystalline systems are strongly influenced by the static relaxation of the surrounding atoms. However, a self-consistent calculation of these relaxational displacements [1] by the *ab initio* electron theory is often very time consuming. Therefore it is highly desirable to obtain at least a good first estimate for these displacements from the forces exerted on the various atoms (obtained either by empirical *ansatze* or by the *ab initio* electron theory) within the linear response theory.

The central quantity in this theory is the zero-frequency limit of the phonon Green's function, the so-called static lattice Green's function [2], $G_{\alpha\beta}(l\kappa, l'\kappa')$, which supplies the connection between the Cartesian β-components $F_\beta(l'\kappa')$ of the forces acting on the atom κ' in the unit cell at the lattice vector l' in the crystal and the α-component $u_\alpha(l\kappa)$ of the displacement of the atom κ in the unit cell at l, via

$$u_\alpha(l\kappa) = \sum_{\beta'l'\kappa'} G_{\alpha\beta}(l\kappa, l'\kappa')F_\beta(l'\kappa'). \tag{1}$$

It may be calculated [2] as the inverse of the force constant matrix Φ, $\mathbf{G} = \Phi^{-1}$, where Φ is defined by

$$\Phi_{\alpha\beta}(l\kappa; l'\kappa') = \left.\frac{\partial^2 V}{\partial u_\alpha(l\kappa)\,\partial u_\beta(l'\kappa')}\right|_0 \tag{2}$$

where V denotes the crystal potential.

The calculation of $\mathbf{G}$ becomes straightforward when considering periodic crystal structures. In this case Φ and $\mathbf{G}$ do not depend on both l and l' but only on the lattice vector separating the two unit cells and therefore it is possible to set l' equal to zero. Instead of calculating

$$G_{\alpha\beta}(\kappa, \kappa'; l) = \left[\Phi_{\tilde\alpha\tilde\beta}(\tilde l\tilde\kappa, \tilde l'\tilde\kappa')\right]^{-1}\Bigg|_{\tilde l=l,\, \tilde l'=0,\, \tilde\kappa=\kappa,\, \tilde\kappa'=\kappa'} \tag{3}$$

which would require the inversion of an infinite matrix, it is then convenient to consider the Fourier series

$$G_{\alpha\beta}(\kappa, \kappa'; l) = \frac{1}{N} \sum_{k} G_{\alpha\beta}(\kappa, \kappa'; k) \exp(ik \cdot l) \tag{4}$$

$$\Phi_{\alpha\beta}(\kappa, \kappa'; l) = \frac{1}{N} \sum_{k} \Phi_{\alpha\beta}(\kappa, \kappa'; k) \exp(ik \cdot l) \tag{5}$$

with N denoting the number of unit cells and with

$$G_{\alpha\beta}(\kappa, \kappa'; k) = \sum_{l} G_{\alpha\beta}(\kappa, \kappa'; l) \exp(-ik \cdot l) \tag{6}$$

$$\Phi_{\alpha\beta}(\kappa, \kappa'; k) = \sum_{l} \Phi_{\alpha\beta}(\kappa, \kappa'; l) \exp(-ik \cdot l). \tag{7}$$

Having determined the $3n \times 3n$ matrix $\Phi(k)$ via equation (7), where n denotes the number of atoms in the unit cell, we can obtain $G(k)$ by inversion of this matrix [2], and then the lattice Green's function in real space may be obtained from equation (4).

The necessary input for the whole calculation, i.e. the real-space force constant matrix $\Phi_{\alpha\beta}(\kappa, \kappa'; l)$, can be determined, e.g. from *ab initio* electron theory or from a Born–von Kármán parametrization of an experimental phonon dispersion spectrum. Phonon spectra measured via inelastic neutron scattering and corresponding Born–von Kármán fits are available in the literature for many materials. In the past, Green's functions have been published for several monatomic face-centred cubic (FCC) and body-centred cubic (BCC) metals for instance by Schober *et al* [3] and MacGillivray and Sholl [4]. In this contribution we apply the method outlined for monatomic systems in [4] to metals with monatomic and diatomic unit cells, namely γ-Fe and FeTi. The force constant matrix in real space is obtained from the experimental phonon dispersion curves of Zarestky and Stassis [6] for γ-Fe and of Buchenau *et al* [7] for FeTi.

As in [4], for the Brillouin zone integration we use the 'special k-point' grids proposed by Chadi and Cohen [5] in equation (4), which do not contain the Γ point, $k = 0$. Note that there is a singularity in $G(k)$ for $k = 0$, since at that point the eigenvalues of $\Phi(k)$ vanish. Because the Γ mode describes a translation of the whole crystal and therefore does not contribute to the crystal potential V we can just exclude the Γ point, which is guaranteed when using the special k-points. In the following we will label the different sets of special k-points by integers $n = 1, 2, \ldots$ where the first set $n = 1$ contains two vectors in the irreducible Brillouin zone of FCC and BCC crystals, namely $k_1 = (2\pi/a)(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $k_2 = (2\pi/a)(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$, or one vector, $k = (2\pi/a)(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, for a simple cubic (SC) crystal. The higher labelled sets $n + 1$ are defined from the nth set by adding the eight vectors $(2\pi/a)(\pm 1/2^{n+2}, \pm 1/2^{n+2}, \pm 1/2^{n+2})$ to each vector of the nth set. Furthermore, the convergence is improved by the scheme of MacGillivray and Sholl [4] who have shown that the Green's function may be extrapolated from the functions calculated with the k-point sets n and $n - 1$, i.e. $g^{(n)}$ and $g^{(n-1)}$, to infinite n via $g_{\text{ext}}^{(n)} = 2g^{(n)} - g^{(n-1)}$. Our programme was tested for some monatomic metals, namely BCC Cr, FCC Cu, and FCC γ-Fe, and for the two former systems we exactly reproduced the results of [4].

More interesting is the comparison (table 1) between our results for γ-Fe and those of Schober [8] who used the method of Gilat and Raubenheimer [9] for the Brillouin zone integration. In both cases, the force constant matrix was determined by a sixth-neighbour Born–von Kármán model of Zarestky and Stassis [6]. The absolute differences between our and Schober's results are in the range 10^{-5} m N^{-1} with a maximum discrepancy of

Table 1. The static Green's function $\mathbf{G}(l)$ of γ-Fe in units of 10^{-2} m N^{-1}; l (in units of the lattice constant a) labels the primitive vectors of the FCC lattice, α and β denote the Cartesian components x, y or z; $g^{(n)}$ and $g_{\text{ext}}^{(n)}$ indicate the elements $G_{\alpha\beta}(l)$ obtained by the summation over the nth k-point set without and with the extrapolation. Schober's results [8] are listed in the last column. Components with zero value are omitted.

l	$\alpha\beta$	g^3	g^4	g_{ext}^4	From [8]
(0, 0, 0)	$xx = yy = zz$	1.696	1.716	1.736	1.742
(1, 1, 0)	$xx = yy$	0.542	0.562	0.582	0.587
	zz	0.468	0.488	0.508	0.513
	xy	0.198	0.198	0.198	0.198
(2, 0, 0)	xx	0.248	0.267	0.286	0.292
	$yy = zz$	0.328	0.348	0.368	0.373
(2, 1, 1)	xx	0.289	0.308	0.327	0.333
	$yy = zz$	0.284	0.304	0.324	0.328
	$xy = xz$	0.085	0.085	0.085	0.085
	yz	0.062	0.063	0.064	0.063
(2, 2, 0)	$xx = yy$	0.284	0.304	0.324	0.328
	zz	0.210	0.230	0.250	0.254
	xy	0.123	0.123	0.123	0.123
(3, 1, 0)	xx	0.162	0.182	0.202	0.206
	yy	0.210	0.230	0.250	0.254
	zz	0.190	0.210	0.230	0.235
	xy	0.038	0.038	0.038	0.038
(2, 2, 2)	$xx = yy = zz$	0.204	0.224	0.244	0.248
	$xy = xz = yz$	0.074	0.074	0.074	0.075
(3, 2, 1)	xx	0.186	0.205	0.224	0.229
	yy	0.190	0.210	0.230	0.233
	zz	0.158	0.178	0.198	0.202
	xy	0.074	0.074	0.074	0.075
	xz	0.043	0.044	0.045	0.044
	yz	0.040	0.040	0.040	0.040
(4, 0, 0)	xx	0.105	0.125	0.145	0.148
	$yy = zz$	0.153	0.173	0.193	0.197
(3, 3, 0)	$xx = yy$	0.173	0.193	0.213	0.216
	zz	0.117	0.137	0.157	0.160
	xy	0.083	0.084	0.084	0.085

6×10^{-5} m N^{-1}, similar to what was found by MacGillivray and Sholl [4] when comparing the data for copper obtained by their method and by Schober's method.

In table 2 the results for $G_{\alpha\beta}(\kappa, \kappa'; l)$ of FeTi are presented up to the primitive lattice vector $l = a(2, 0, 0)$ of the SC lattice with the basis atoms Ti at $l + a(0, 0, 0)$ and Fe at $l + a(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The force constant matrix was determined by the fourth-neighbour Born–

Table 2. The static Green's function $\mathbf{G}(l)$ of FeTi in units of 10^{-2} m N^{-1}; l (in units of the lattice constant a) is a primitive vector of the sc lattice, κ and κ' denote the two atoms considered, Ti (1) or Fe (2), α and β the Cartesian components x, y or z; $g^{(n)}$ and $g_{\text{ext}}^{(n)}$ indicate the elements $G_{\alpha\beta}^{mn}(l)$ obtained with the summation over the nth k-point set without and with the extrapolation. Components with zero value are omitted.

l	$\kappa\kappa'$; $\alpha\beta$	g^2	g^3	g^4	g_{ext}^3	g_{ext}^4
(0, 0, 0)	1 1 $xx = yy = zz$	0.909	0.945	0.962	0.981	0.979
	12 $xx = yy = zz$	0.226	0.260	0.278	0.294	0.296
	12 $xy = xz = yz$	0.028	0.027	0.027	0.026	0.027
	22 $xx = yy = zz$	0.890	0.924	0.941	0.958	0.958
(1, 0, 0)	11 xx	0.376	0.413	0.431	0.450	0.449
	11 $yy = zz$	0.111	0.145	0.162	0.179	0.179
	12 xx	0.132	0.169	0.187	0.206	0.205
	12 $xy = xz$	0.020	0.019	0.019	0.018	0.019
	12 $yy = zz$	0.072	0.103	0.120	0.134	0.137
	12 yz	0.004	0.004	0.004	0.004	0.004
	22 xx	0.279	0.315	0.332	0.351	0.349
	22 $yy = zz$	0.189	0.221	0.238	0.253	0.255
(1, 1, 0)	11 $xx = yy$	0.118	0.153	0.171	0.188	0.189
	11 xy	0.029	0.028	0.027	0.027	0.026
	11 zz	0.090	0.122	0.139	0.154	0.156
	12 $xx = yy$	0.060	0.093	0.110	0.126	0.127
	12 xy	0.024	0.022	0.021	0.020	0.022
	12 $xz = yz$	0.007	0.006	0.006	0.005	0.006
	12 $zx = zy$	0.007	0.006	0.006	0.005	0.006
	12 zz	0.039	0.067	0.084	0.095	0.101
	22 $xx = yy$	0.135	0.168	0.185	0.201	0.202
	22 xy	0.040	0.039	0.039	0.038	0.039
	22 zz	0.088	0.118	0.135	0.148	0.152
(1, 1, 1)	11 $xx = yy = zz$	0.080	0.113	0.130	0.146	0.147
	11 $xy = xz = yz$	0.015	0.014	0.014	0.013	0.014
	12 $xx = yy = zz$	0.035	0.064	0.081	0.093	0.098
	12 $xy = xz = yz$	0.014	0.012	0.011	0.010	0.010
	22 $xx = yy = zz$	0.085	0.116	0.133	0.147	0.150
	22 $xy = xz = yz$	0.021	0.020	0.020	0.019	0.020
(2, 0, 0)	11 xx	0.163	0.206	0.224	0.249	0.242
	11 $yy = zz$	0.044	0.073	0.089	0.102	0.105
	12 xx	0.067	0.110	0.129	0.153	0.148
	12 $xy = xz$	0.012	0.010	0.010	0.008	0.010
	12 $yx = zx$	0.009	0.007	0.007	0.005	0.007
	12 $yy = zz$	0.026	0.052	0.067	0.078	0.082
	12 $yz = zy$	0.001	0.001	0.001	0.001	0.001
	22 xx	0.113	0.153	0.171	0.193	0.189
	22 $yy = zz$	0.053	0.080	0.097	0.107	0.114

von Kármán model of Buchenau *et al* [7]. As could already be expected from the force constants [7], matrix elements of the lattice Green's function corresponding to Fe and Ti atoms, respectively, are distinctly different, in contrast, e.g., to the elastic Green's function, and for both they differ from matrix elements of BCC Cr [4] which is isoelectronic to FeTi.

This indicates that for lattice relaxations in the intermetallic compound the use of the proper lattice Green's function is presumably essential.

To summarize, in this work we have extended and applied the scheme of MacGillivray and Sholl [4] for the calculation of the static lattice Green's function to the case of crystalline systems with more than one atom in the unit cell. Numerical results for γ-Fe and FeTi, which we intend to use for the consideration of the self-trapped states of hydrogen isotopes (see, e.g., [10]), are provided.

Acknowledgments

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