The interstitial electron model for metals—a critical appraisal

G D Barrera†, N L Allan and T H K Barron

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

Abstract. The interstitial electron model (IEM) of Li and Goddard has reproduced with good success the phonon dispersion curves of many face-centred cubic (FCC) metals. The key feature of the model is the location of light interstitial particles in the tetrahedral holes of the structure. In this paper the validity of the model is further tested: (i) by applying it to three additional FCC metals, β-Co, La and Th; (ii) by using it to calculate anharmonic properties; (iii) by considering extensions to hexagonal close-packed (HCP) and body-centred cubic (BCC) metals. These demanding tests reveal several shortcomings. There is good agreement for the experimental dispersion curves of β-Co and La, but only if additional interactions and input data are used in the fitting; the agreement for Th is only fair. Applied to anharmonic properties of FCC metals, the IEM cannot explain simultaneously both the temperature dependence of the Grüneisen function and the pressure dependence of the second-order elastic stiffnesses. Other than for Mg and α-Co, it cannot reproduce the frequency dispersion curves of HCP metals. Its use for BCC systems is impractical due to the large number of parameters required. Even where the model is successful in predicting dispersion curves, equally satisfactory agreement can be obtained with a valence force-field, sometimes with fewer adjustable parameters.

1. Introduction

The use of pair potentials alone to represent the interatomic forces in metals has serious deficiencies, including the inability to explain violations of the Cauchy relations between elastic stiffnesses, or even the qualitative form of some phonon dispersion curves. The interstitial electron model (IEM) of Li and Goddard (1989, 1993) surmounts this difficulty by introducing light interstitial particles, which interact both with each other and the metal atoms through short-range pair potentials. This model was suggested by *ab initio* calculations on small metal clusters, which show a concentration of the valence electron density at interstitial regions between the atoms rather than around individual atomic centres (McAdon and Goddard 1985, 1987—see also Tornaghi *et al* 1991, 1992, Lepetit *et al* 1990, 1992). Li and Goddard placed the interstitial particles in tetrahedral holes of the face-centred cubic (FCC) structure, where previous generalized valence bond calculations (McAdon and Goddard 1985, 1987) had indicated an accumulation of charge. Since these sites (unlike the octahedral holes) are not centres of inversion symmetry, the model no longer has to satisfy the Cauchy relations, and so the interstitial particles provide effective non-central forces between the ions. For simplicity, the metal atoms and interstitials were taken as uncharged, and account was taken only of nearest-neighbour ion–ion, ion–interstitial and interstitial–interstitial pair interactions. The condition of zero pressure then gave five independent force constants, which were fitted to the three elastic stiffnesses and the two frequencies at

† Permanent address: Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Departamento de Química Inorgánica, Analítica y Química Física, Pabellón 2, Ciudad Universitaria, 1428 Buenos Aires, Argentina.

the X point. The calculated phonon dispersion curves for a range of FCC metals were in good agreement with experiment. Schultz and Messmer (1992) have also used the model to calculate dispersion curves of the FCC alloy Ni_3Al, and again the agreement with experiment was satisfactory.

In this paper we submit this model to further tests. Theoretical methods are described in section 2. We then extend the calculations to three additional FCC metals (section 3), including the f-block metals La and Th. Next we examine the ability of the IEM to account for essentially anharmonic properties, namely the pressure dependence of the second-order elastic constants and the temperature dependence of the Grüneisen function (section 4).

A further test is to apply the IEM to metals with structures other than FCC. In section 5 we consider hexagonal close-packed (HCP) metals. The theory is more complicated than for FCC systems; not only are there more species in the unit cell, but also the position of the interstitial particles in the tetrahedral holes is no longer fixed by symmetry. In section 6 we discuss the IEM critically, comparing it with other models of comparable simplicity.

2. Theoretical methods

The IEM has been described in detail for FCC metals by Li and Goddard (1989, 1993), and we follow their notation. Interstitial particles are placed in the tetrahedral holes. Allowing only for two-body interactions, there are three independent potentials, $\phi_{i-i}(r)$, $\phi_{e-i}(r)$ and $\phi_{e-e}(r)$ representing ion–ion, ion–interstitial and interstitial–interstitial interactions respectively. For harmonic properties, it is necessary to know the values of $\phi' = d\phi/dr$ and $\phi'' = d^2\phi/dr^2$ at the appropriate separations. Further parameters ($\phi''' = d^3\phi/dr^3$) are needed for anharmonic properties.

The space group of the FCC metals is O_h^5 ($Fm3m$). There are three particles in the primitive cell—one ion at $(0,0,0)$ and two interstitial electrons in tetrahedral holes at $(a/4, a/4, a/4)$ and $(3a/4, 3a/4, 3a/4)$. If nearest-neighbour interactions alone are considered, only five of the resulting six parameters are independent, because of the equilibrium condition; these can be determined analytically from the three elastic constants and two vibrational frequencies (e.g., at the X point). Further harmonic properties such as the phonon dispersion relations are then calculated using these parameters. For anharmonic properties, values for $\phi''' = d^3\phi/dr^3$ can be obtained by fitting either third-order elastic constants or the pressure derivatives of the second-order elastic constants. The possibility of including interactions other than those between nearest neighbours is dealt with in section 3.

The space group of HCP metals is D_{6h}^4 ($P6_3/mmc$). There are six particles in the unit cell—two ions at $(0,0,0)$ and $(a/2, a/2\sqrt{3}, c/2)$, and four interstitial particles in tetrahedral holes at $(0, a/\sqrt{3}, \pm hc)$ and $(0, 0, (\frac{1}{2} \pm h)c)$. Only for ideal packing ($c/a = \sqrt{8/3}$) can the interstitial positions be fixed by the regularity of the tetrahedron, when $h = 3/8$. For real metals h is treated as an additional parameter (see figure 1). The HCP model is appreciably more complicated than the FCC. Even with ideal packing, there are three distinct interstitial–interstitial distances and one ion–interstitial distance smaller than the nearest-neighbour ion–ion separation; there are more such distances when the packing is non-ideal. We have investigated the effect of including various numbers of interactions (section 5).

The space group of BCC metals is O_h^9 ($Im3m$). There are seven particles in the primitive unit cell—one ion at $(0,0,0)$ and six tetrahedral interstitial positions at $(0, a/2, \pm a/4)$, $(\pm a/4, 0, a/2)$, $(a/2, \pm a/4, 0)$. There are now many interparticle separations—six distinct interstitial–interstitial and one ion–interstitial distances not greater than that between nearest-neighbour ions, giving 16 parameters altogether. This is too many for practical applications, and so we have not pursued this further.
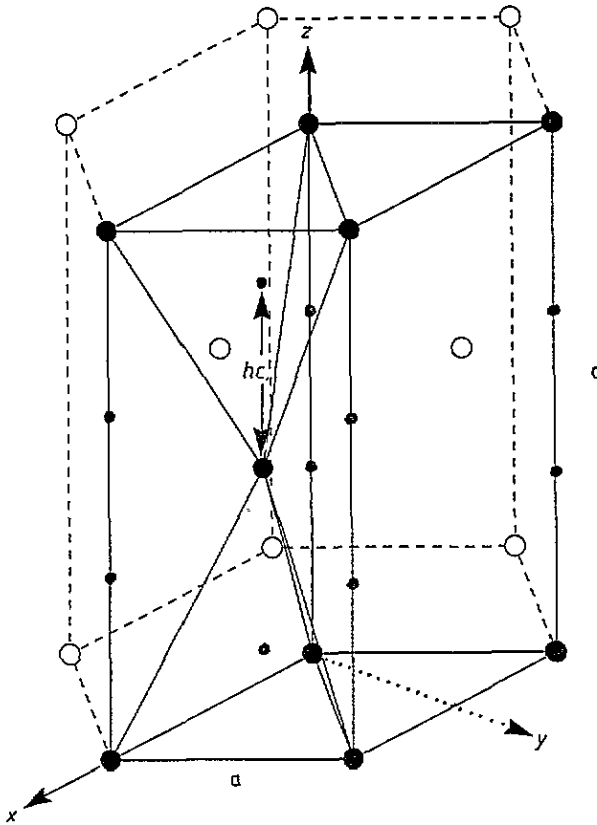
Figure 1. Part of the HCP lattice showing tetrahedral sites for interstitial particles. The interstitial positions are denoted by small black circles. The heights of these positions are determined by the variable parameter h.

3. FCC metals—harmonic properties

We have examined three FCC metals not considered by Li and Goddard—β-Co, La and Th. Following their procedure (in which only nearest-neighbour interactions are considered), the six potential parameters were obtained using the data of table 1 and the two phonon frequencies at the X point (Reese *et al* 1973, Svensson *et al* 1979, Stassis *et al* 1982). These parameters were then used to calculate the phonon dispersion curves shown in figure 2. Surprisingly, the agreement with experiment is much poorer for all three metals than for those systems (Al, Ca, Sr, γ-Fe, Ni, Pd, Pt, Cu, Ag and Au) considered by Li and Goddard. We therefore added to their model one further interstitial–interstitial interaction at a distance of $a/\sqrt{2}$ (which is also the nearest-neighbour ion–ion distance), and fitted the model in a different way. We used all the experimental phonon data, and obtained the potential parameters by least-squares fitting. The resulting phonon dispersion curves, which overall are in rather better agreement with experiment, are also shown in figure 2. Even so, only for La were the fitted frequencies at the points X and L within experimental error. For Th and β-Co the best fits resulted in differences at the X point between theory and experiment of $\approx 6.0\%$ and $\approx 3.0\%$ respectively. The final set of potential parameters obtained by
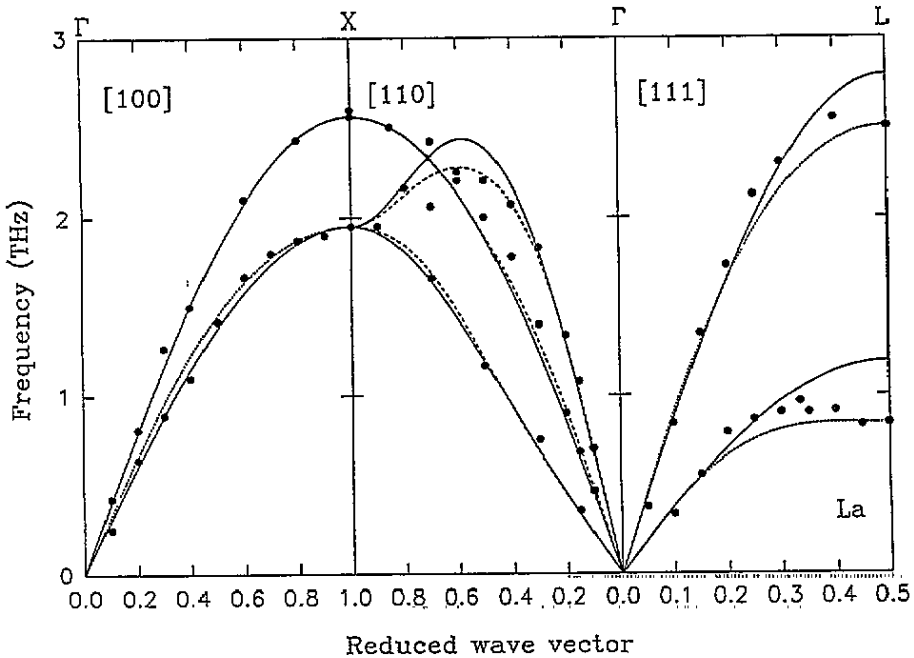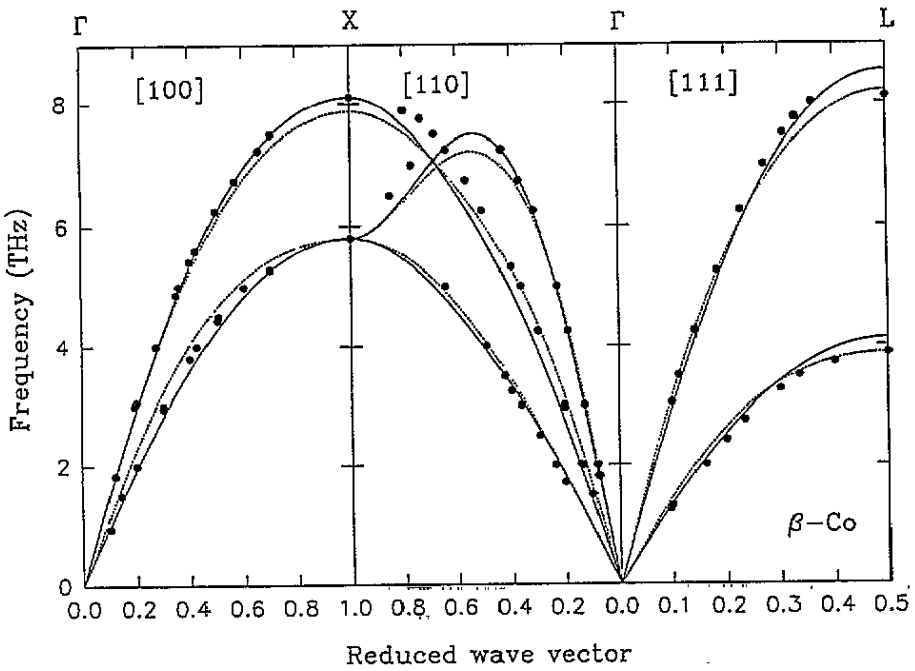
Figure 2. Experimental (points) phonon dispersion curves for β-Co (Svensson *et al* 1979), La (Stassis *et al* 1982) and Th (Reese *et al* 1973). The solid lines are the curves calculated from the six-parameter IEM model using the lattice spacings, elastic constants and the frequencies at the X point in the analysis. The dashed lines are curves calculated from an eight-parameter model, using all the experimental data and a least-squares fitting procedure to obtain the potential parameters.

Figure 2. (Continued)

Table 1. The lattice constants, a_0 (Å), and the elastic stiffnesses, C_{11}, C_{22} and C_{33} (10^{11} Pa), used to parametrize the IEM for β-Co (Hearmon 1979), La (Stassis 1982) and Th (Hearmon 1979).
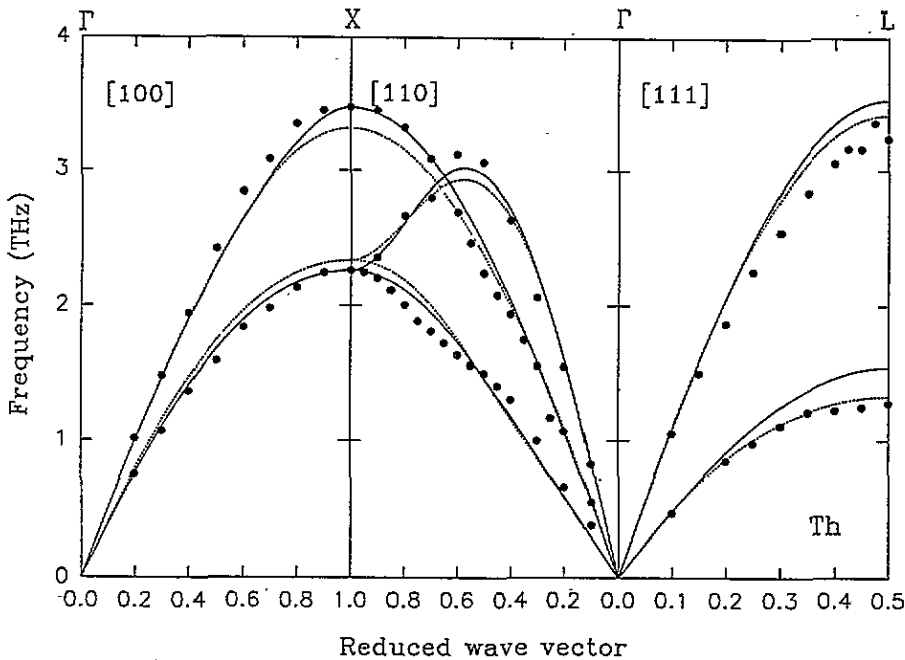
Metal	a_0	C_{11}	C_{12}	C_{44}
β-Co	3.54	2.60	1.60	1.10
La	5.30	2.85	2.04	1.65
Th	5.08	7.70	5.09	4.55

Table 2. The final potential parameters for β-Co. La and Th. In specifying the interactions, i refers to an ion, e to an interstitial electron. The value of r given (in Å) for each interaction denotes the relevant interparticle separation. The units of ϕ'/r and ϕ'' are N m^{-1}.

| Interaction | β-Co | | | La | | | Th | | |
	r	ϕ'/r	ϕ''	r	ϕ'/r	ϕ''	r	ϕ'/r	ϕ''
i–e	1.533	16.460	23.134	2.295	10.634	11.587	2.200	1.324	1.682
e–e	1.770	−3.175	−4.596	2.650	−2.632	5.589	2.540	1.581	−4.596
e–e	2.503	1.026	1.073	3.745	0.616	2.159	3.592	0.614	1.073
i–i	2.503	−8.694	21.476	3.745	−5.233	1.862	3.592	−2.680	22.027

least-squares fitting are listed in table 2. The agreement with experiment is not improved appreciably by including additional interactions.

The lattice contribution to the heat capacity predicted by all the models is in good agreement with experiment for β-Co and Th up to $\theta_D/4$ (where θ_D is the Debye temperature). At higher temperatures anharmonic contributions become important, and

at 300 K, differences between experimental and theoretical C_V values are about 11% and 8% for Th and β-Co respectively. We have not found any heat capacity data for La.

4. FCC metals—anharmonic properties

Here we consider both the higher-order elasticity and the thermal expansion. Rather than calculating the thermal expansion coeffficient β itself, we derive the lattice contribution to the Grüneisen function γ, which is more suitable for graphical comparison of experiment with theory. γ gives the rate of increase of pressure with internal energy density,

$$\gamma = [\partial P/\partial (U/V)]_V.$$

It is derived from experimental data by means of the identity

$$\gamma = \beta V/\chi_S C_P$$

where C_P is the heat capacity at constant pressure and χ_S the adiabatic compressibility. Theoretically, in the quasiharmonic approximation (see, e.g., Barron *et al* 1980), the lattice contribution is

$$\gamma_{\text{vib}} = \sum_j \gamma_j c_j \Big/ \sum_j c_j$$

where c_j is the contribution to the heat capacity of the jth normal mode with frequency ν_j, and γ_j is the mode Grüneisen parameter defined by

$$\gamma_j = -\mathrm{d}\ln\nu_j/\mathrm{d}\ln V.$$

We consider specifically Cu, Ag and Au because Li and Goddard found that the IEM gave dispersion curves for these metals in excellent agreement with experiment. The calculation now involves the additional parameters

$$\phi''' = \mathrm{d}^3\phi/\mathrm{d}r^3.$$

These were obtained from the experimental pressure derivatives of the second-order stiffnesses, C'_{ij}, which are linear functions of the ϕ'''. The elastic data (with a_0) are listed in table 3, and the resulting potential parameters in table 4.

Table 3. The lattice constants, a_0 (Å), the second-order elastic constants (10^{11} Pa) (Schober and Dederichs 1981) and their pressure derivatives (dimensionless) (Daniels and Smith 1958), used to parametrize the IEM for Cu, Ag and Au.

Metal	a_0	C_{11}	C_{12}	C_{44}	C'_{11}	C'_{12}	C'_{44}
Cu	3.615	1.684	1.214	0.754	5.91	5.03	2.63
Ag	4.086	1.240	0.934	0.461	5.12	3.61	3.04
Au	4.078	1.930	1.634	0.420	7.01	6.14	1.79

Table 4. The final potential parameters for Cu, Ag and Au. For the notation used see the caption to table 2. The units of ϕ'/r, ϕ'' and $r\phi'''$ are N m^{-1}.

Interaction	Cu				Ag				Au			
	r	ϕ'/r	ϕ''	$r\phi'''$	r	ϕ'/r	ϕ''	$r\phi'''$	r	ϕ'/r	ϕ''	$r\phi'''$
i–i	2.556	−6.300	4.633	−591.30	2.889	−3.526	3.580	−711.95	2.884	−6.904	−15.328	−735.98
i–e	1.565	12.327	61.745	118.88	1.769	6.344	55.296	644.81	1.766	15.798	132.088	−391.17
e–e	1.565	0.272	3.676	98.53	1.769	0.708	4.159	136.05	1.766	−1.995	8.845	64.60

The value of the lattice contribution to the Grüneisen function in the limit $T \to 0$, γ_0, is determined by the C'_{ij} independently of the model, since in this limit only elastic modes contribute to thermodynamic properties. Values of γ at higher temperatures, however, are model-dependent, and were calculated by means of first-order perturbation theory (see, e.g., Wallace 1972, Barron and Pasternak 1987). The calculated high-temperature limits, γ_∞, are considerably higher than those measured experimentally (table 5), revealing a much greater variation of $\gamma(T)$ with temperature than that observed (see figure 3 for the case of Cu). In an attempt to improve the agreement, we also tried a least-squares procedure to obtain the ϕ''', including the experimental values of γ_∞ in the fit. This was largely unsuccessful. For Cu, the fitted value of γ_∞ decreased only to 2.24, while the fitted C'_{44} increased by 16% from 2.27 to 2.63. For each metal, the difference between γ_∞ and γ_0 is still much larger in the IEM than that observed.

Table 5. Experimental values (White and Collins 1972) of the Grüneisen functions γ_∞ and γ_0, corresponding to the limits $T \to \infty$ and $T \to 0$ respectively, for Cu, Ag and Au. The calculated values of γ_∞ are also given.

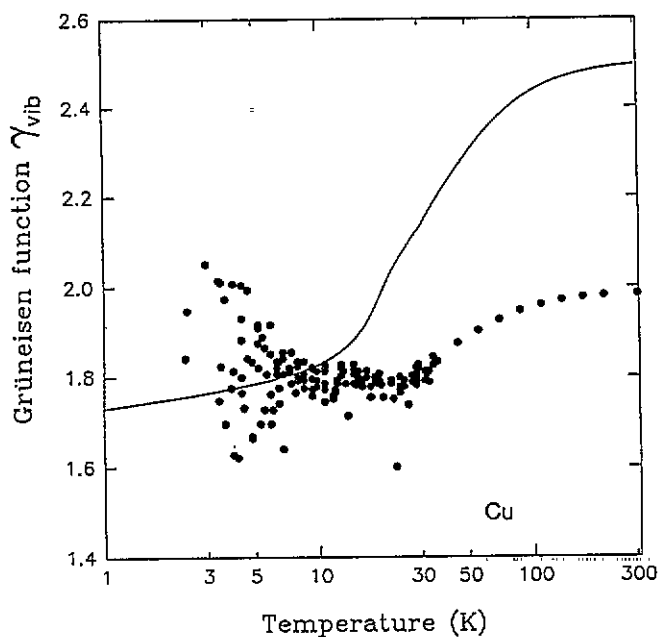|	Cu	Ag	Au
γ_∞ (calc.)	2.50	3.26	3.41
γ_∞ (exp.)	1.98	2.38	2.96
γ_0 (exp.)	1.738	2.14	2.91

Figure 3. The calculated and experimental (White and Collins 1972) variation of $\gamma_{vib}(T)$ with T for copper.

5. HCP metals—harmonic properties

We have considered a wide range of HCP metals. Even with a potential cut-off just larger than the nearest-neighbour ion–ion separation there are more interactions to consider than for FCC metals.

In our first calculations on HCP metals (not ideally packed) we took account of two ion–ion interactions (corresponding to the two smallest separations of 0.319 Å and 0.321 Å for Mg), the ion–interstitial interaction (at 0.196 Å for Mg) and two interstitial–interstitial interactions (0.128 Å and 0.227 Å for Mg). This gives a total of ten potential parameters, of which seven are independent because there are three equations for mechanical equilibrium. A least-squares fit to the elastic constants given in table 6, together with selected phonon frequencies, gave the model parameters listed in table 7.

Table 6. The lattice constants a_0 (Å) and c_0 (Å), and the elastic stiffnesses (10^{11} Pa), used to parametrize the IEM for Mg and α-Co (Schober and Dederichs 1981).

Metal	a_0	c_0	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}
Mg	3.21	5.21	5.943	2.561	2.144	6.241	1.641
α-Co	2.51	4.07	30.63	16.51	10.19	35.74	7.53

Table 7. The final potential parameters for Mg and α-Co. For the notation used see the caption to table 2.

Interaction	Mg			α-Co		
	r	ϕ'/r	ϕ''	r	ϕ'/r	ϕ''
e–e	1.287	1.289	−1.308	1.003	10.274	6.565
i–e	1.962	−0.138	3.279	1.534	−2.694	35.195
e–e	2.275	0.421	−1.996	1.779	3.354	3.852
i–i	3.197	−0.144	10.824	2.498	−0.347	30.646
i–i	3.210	−0.004	10.040	2.510	0.794	32.383

The final dispersion curves for Mg and α-Co are shown in figure 4. These are in reasonable agreement with experiment. Extending the potential to include the second set of interstitial–interstitial interactions (at 0.319 Å and 0.321 Å for Mg) had only a very small effect on the final curves, as did varying h.

We also tried explicit forms for the potentials (Lennard-Jones, Buckingham and a Buckingham form with additional r^{-n} terms) and adapted the least-squares procedure to determine the corresponding parameters. The results obtained showed no improvement.

The IEM failed to give even a qualitative description of the phonon dispersion curves for all the other HCP metals we examined (Zn, Zr, Sc, Y and Ho).

6. Discussion and conclusions

We have applied a series of stringent tests to the IEM. In general it gives a good description of the dispersion curves of FCC metals, but no better than can be obtained from other models of comparable simplicity. In particular one of us (Barrera 1994) has found that the dispersion
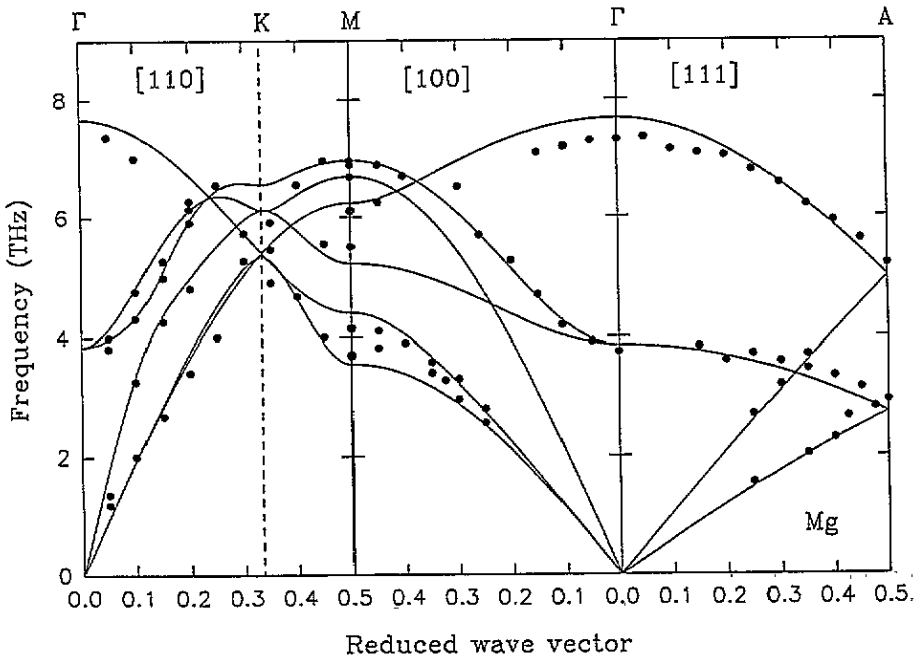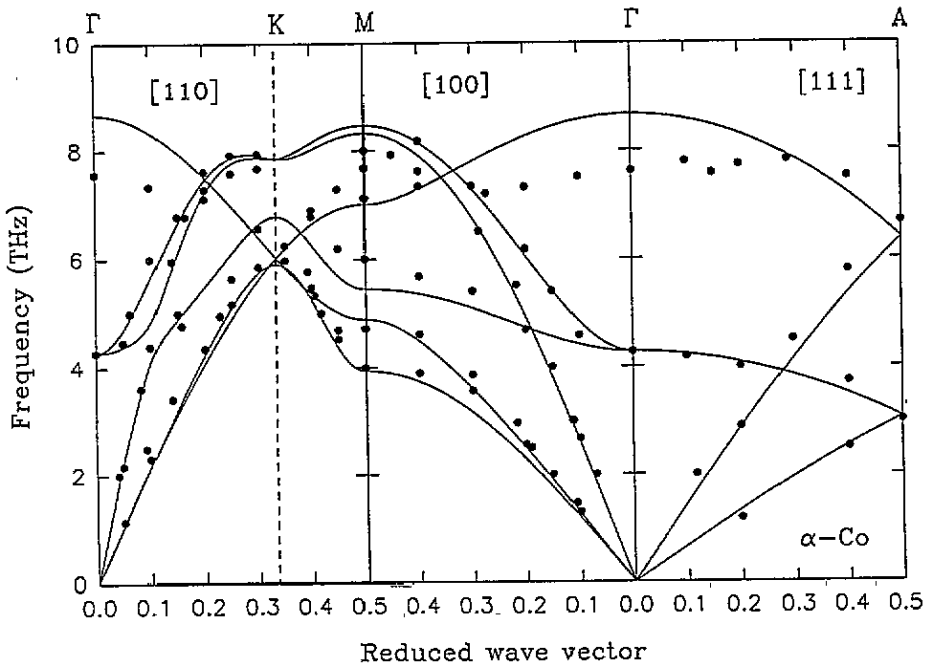
Figure 4. Experimental (points) phonon dispersion curves for α-Co (Wakabayashi *et al* 1982) and Mg (Stassis *et al* 1982). The solid lines are the curves calculated from the fitted ten-parameter IEM model.

curves of all the FCC metals so far treated by the IEM can be fitted equally well or better by a five-parameter model which includes an angle potential in addition to pair potentials. This model can also give good agreement with anharmonic data. The IEM fails other tests badly, as detailed below.

(i) It is impossible to get a good fit to both $\partial C_{\lambda\mu}/\partial P$ and $\gamma(T)$ of FCC noble metals, primarily because of a large variation in $\gamma(T)$ which persists even when all ϕ''' parameters are set to zero. In comparison a model which considers only nearest-neighbour pair potentials (Barron 1955) gives $\gamma_\infty - \gamma_0 \approx 0.3$, in qualitative agreement with experiment. A three-body potential model with three harmonic and one anharmonic parameter has been successful in reproducing both the pressure dependence of the elastic constants and the temperature dependence of the Grüneisen function (Barrera and Batana 1993a, b).

(ii) For HCP metals, it has been possible to obtain a reasonable fit to the dispersion curves and elastic constants only for Mg and β-Co, the same metals that historically have been found relatively easy to fit using other models (see, e.g., work cited by Schober and Dederichs 1981). The potential for β-Co is not transferable to α-Co.

(iii) There appear to be no clear trends in the values of the parameters from one metal to another. This is in marked contrast to parameters in other potential models incorporating three-body forces (e.g. Barrera and Batana 1993a, b).

It is of course possible that some of these shortcomings could be remedied by modifications of the model. The number of parameters for HCP and BCC structures could be reduced by further approximations. Future work could include a systematic study of such an approach, including the use of explicit forms for the pair potential and the incorporation of charged particles.

As pointed out by Li and Goddard, the IEM has a direct physical appeal similar to the shell model (Dick and Overhauser 1958, Cochran 1971), in that the forces are represented by a simple mechanical model. Nevertheless there are important distinctions between the two. The shell model can be seen to represent two interrelated effects—the polarization of the ions by electric fields and the distortion caused by overlap—and so to some extent genuinely represents the underlying physics. The IEM is on much less certain ground. Not only may it overemphasize the concentration of electron density at tetrahedral sites, but also there is no convincing evidence, either experimental or theoretical, that the IEM represents how the electrons respond to the motion of the ions. The IEM appears to be chiefly of value for its own sake, in that it represents a new type of potential which may behave in ways different from all other known models. In this context the behaviour of $\gamma(T)$ is interesting, as it provides a rare example of the effect of anharmonicity in non-central components of the force-field.

References

Barrera G D 1994 private communication

Barrera G D and Batana A 1993a *Phys. Rev.* B **47** 8588
—— 1993b *Phys. Status Solidi* b **179** 59
Barron T H K 1955 *Phil. Mag.* **46** 720
Barron T H K, Collins J G and White G K 1980 *Adv. Phys.* **29** 609
Barron T H K and Pasternak A 1987 *J. Phys. C: Solid State Phys.* **20** 215
Cochran W 1971 *Crit. Rev. Solid State Sci.* **2** 1
Daniels W B and Smith C S 1958 *Phys. Rev.* **111** 112
Dick B G and Overhauser A W 1958 *Phys. Rev.* **112** 90
Hearmon R F S 1979 *Landolt–Börnstein New Series* Group III, vol 11 (Berlin: Springer)
Lepetit M B, Aprà E, Malrieu J P and Dovesi R 1992 *Phys. Rev.* B **46** 12974
Lepetit M B, Malrieu J P and Spiegelmann F 1990 *Phys. Rev.* B **41** 8093
Li M and Goddard W A 1989 *Phys. Rev.* B **40** 12155
—— 1993 *J. Chem. Phys.* **98** 7995
McAdon M H and Goddard W A 1985 *Phys. Rev. Lett.* **55** 2563
—— 1987 *J. Phys. Chem.* **91** 2607
Pynn R and Squires G L 1972 *Proc. R. Soc.* A **326** 347
Reese R A, Sinha S K and Peterson S K 1973 *Phys. Rev.* B **8** 1332
Schober H R and Dederichs H 1981 *Landolt–Börnstein New Series* Group III, vol 13a (Berlin: Springer)
Schultz P A and Messmer R P 1992 *Phys. Rev.* B **45** 7467
Stassis C, Loong C K and Zarestky J 1982 *Phys. Rev.* B **26** 5426
Svensson E C, Powell B M, Woods A D and Teuchert W D 1979 *Can. J. Phys.* **57** 253
Tornaghi E, Cooper D L, Gerratt J and Raimondi M 1991 *Croatica Chem. Acta* **64** 429
Tornaghi E, Cooper D L, Gerratt J, Raimondi M and Sironi M 1992 *J. Mol. Struct. (Theochem.)* **259** 383
Wakabayashi N, Scherm R H and Smith H G 1982 *Phys. Rev.* B **25** 5122
Wallace D C 1972 *Thermodynamics of Crystals* (New York: Wiley)
White G K and Collins J G 1972 *J. Low Temp. Phys.* **1** 43