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Lattice dynamics of face-centered-cubic $Co_{0.92}Fe_{0.08}$

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The room-temperature lattice dynamics of a crystal of $Co_{0.92}Fe_{0.08}$ were studied with a view to understanding the fcc-hcp transition which occurs in pure Co at ~415°C. Because the martensitic transformation lies well below 77°K for this alloy, no anomalous neutron scattering was observed. We did, however, measure a complete set of phonon dispersion curves and obtained a set of Born–von Kármán force constants from which the usual thermodynamic data have been derived. As the masses of Fe and Co are so similar, these results should represent the lattice dynamics for fcc cobalt.

I. INTRODUCTION

Pure cobalt undergoes a first-order martensitic phase transformation from a high-temperature face-centered-cubic (fcc) structure to a hexagonal close-packed (hcp) structure at $T_M \sim 420$ °C.[1] Recent Mössbauer measurements[2] on a Co–7-wt%-Fe sample showed a decrease in T_M to ~140 °C and an anomalous decrease of Debye-Waller factor at the phase transition which was interpreted as an increase in the root-mean-square displacement of the atoms due to a change in interatomic force constants. This suggests that some form of lattice softening[3] takes place which characterizes the transition from fcc to hcp. The purpose of this study was thus to investigate the lattice-dynamical properties of fcc cobalt in order to gain insight into the mechanism of the martensitic phase transformation.

Pure single-crystal fcc cobalt has not been studied to date both because the 420 °C phase transformation is usually destructive and because Co is a strong neutron absorber. However, it is well known that by alloying with a small concentration of Fe or Ni the martensitic transition temperature is dramatically reduced[1] (to well below room temperature) and the fcc alloy can be conveniently studied. Since Fe, Ni, and Co all have similar atomic masses and sizes, the phonon groups of our $Co_{0.92}Fe_{0.08}$ alloy should be well defined and the measured dispersion relations should be representative for pure Co. As these masses and sizes are so similar we are further led to suspect an electronic basis for the structural instability because of the very strong composition dependence of the transition temperature.

If the Mössbauer result is a general one for the fcc-hcp transformation in Co alloys, one would expect to observe similar premonitory dynamical effects in the inelastic neutron scattering. Assuming these effects to be similar to a true lattice softening, one should then expect for the appropriate phonons to observe a frequency lowering as the transition temperature (T_M) is approached from above or below.[4] If, however, the time scale for the premonitory softening is too long for the neutron resolution ($\tau > 0.2 \times 10^{11}$ sec^{-1}), but short enough to appear as a dynamical effect in the Mössbauer study, we would expect to observe a build up of elastic or quasielastic intensity at the appropriate phonon wave vectors.

Figure 1 shows the relationship between the fcc and hcp structure viewed here as a stacking of (111) planes in the fcc phase with a sequence of *ABC ABC ABC* versus the hcp stacking of *AB AB AB*.[5] The transformation between the two is accomplished as indicated by the displacements given by two waves of wavelengths $6d_{(111)}$ and $3d_{(111)}$, where $d_{(111)}$ is the (111) interplanar spacing.[5] The amplitudes of these waves are related by $\sqrt{3}$ to give precisely the hcp stacking from the fcc sequence. Both waves have wave vectors along the $\langle 111 \rangle$ directions with polarization in the $\langle 112 \rangle$ directions. The actual displacements required, however, are large ($\sim 0.41 a_0$, where a_0 is the cubic lattice parameter) as the close-packed planes have to roll over each other past a potential barrier caused by the bridge between close-packed atoms in the planes. The transformation is, therefore, first order both because of the large displacements required and because of the above barrier.

A clear way of relating the two structures is to display their reciprocal lattices together as in Fig. 2. The $[111]_{\text{cub}}$ direction in the fcc phase becomes the $[00.1]_{\text{hex}}$ direction in the hexagonal phase. Similarly, the $[\bar{1}\bar{1}2]_{\text{cub}}$ direction becomes $[01.0]_{\text{hex}}$. In this zone the hcp reflections that are not also fcc appear as spots flanking the fcc re-

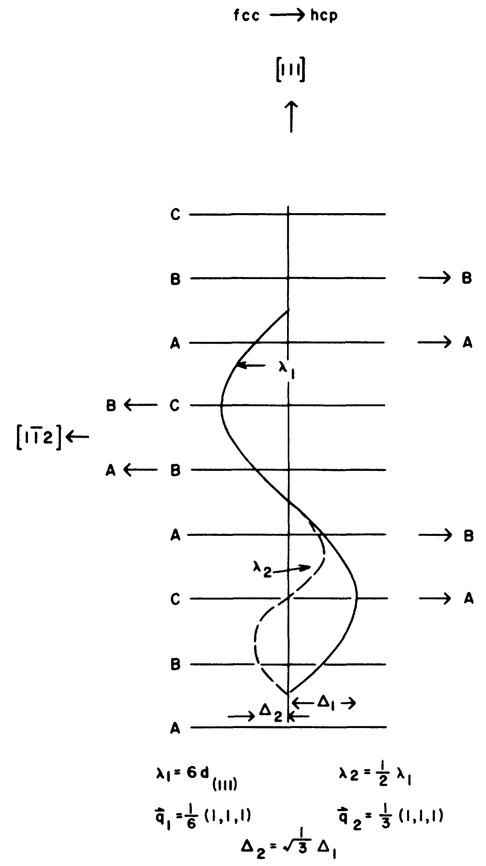

FIG. 1. Stacking of the atomic planes along the [111] direction and the motion necessary to take the fcc *ABC ABC* stacking into a hcp *AB AB AB* stacking. The two waves are 180° out of phase.

flection translated along [111] by $\frac{1}{6}[\tau(111)]$ or $\frac{1}{3}[\tau(111)]$. $\tau(111)$ is the reciprocal-lattice spacing in the [111] direction for the fcc structure. The hcp reflections are thereby seen to be given simply by the two static or condensed waves of Fig. 1 whose amplitudes have opposite signs (a 180° phase shift). The premonitory effects observed in the Mössbauer study should thus be detectable at these wave vectors either as a lattice softening for transverse [111] wave polarized along $[\overline{11}2]$ or, as quasielastic scattering whose intensity increases at T_M is approached.

II. EXPERIMENT

The experiments were performed on a single crystal of $Co_{0.92}Fe_{0.08}$ which is stable in the fcc phase at room temperature. This turned out to be an unfortunate choice in that for this Fe percentage T_M is most likely below 0°K,[1] and no transformation was observed. The result of Bokshtein *et al.*[2] becomes, therefore, surprising. It is not that we question the existence of a transformation at 140 °C. Rather, we are led, via our own results and Ref. 1, to suspect their composition of being substantially lower in Fe. Nonetheless, as noted above, because the masses and sizes of Fe and Co are so similar the lattice-dynamical results should be a very good approximation to pure cobalt. Cobalt has a large absorption cross section for thermal neutrons (~ 10 times larger than for nickel) and is a weak scatterer (~ 16 times weaker than nickel) which explains the lack of data on single crystals of Co.

Two different samples of $Co_{0.92}Fe_{0.08}$ of approximately the same rectangular shape with dimensions $1\frac{1}{4}\times\frac{5}{8}\times\frac{1}{8}$ in.^{3} were used. The long axis was parallel to the [110] direction. These crystals had a mosaic spread of 5′ and were, in fact, purchased for use as a neutron polarizer.

The inelastic scattering experiments were performed at the High Flux Beam Reactor at Brookhaven National Laboratory. Most of the data was taken at a fixed analyzer energy of 14.8 meV and a varying incident energy. The horizontal collimation was 40′ throughout the instrument. Pyrolitic graphite was used as a monochromator and analyzer and a pyrolytic-graphite filter was placed in the scattered beam to eliminate higher-order contamination. Some data was also taken with a fixed incoming energy of 41.0 meV.

III. RESULTS

The measurements were performed at room temperature and 77 °K. At lower temperatures we saw no change in the phonon spectra other than a decrease in intensity due to a change in the occupa-

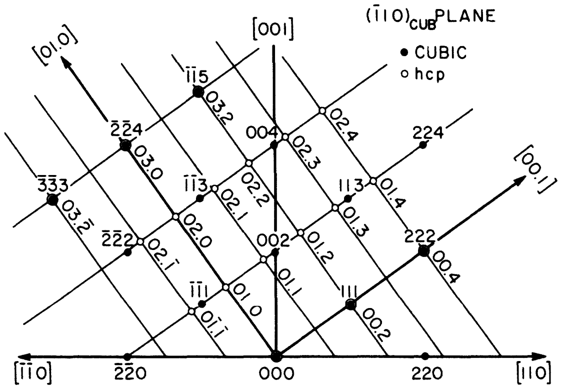

FIG. 2. Reciprocal lattice of the fcc and hcp structure. The solid dots represent fcc reflections and the open circles represent the hcp reflection. Note that $[111]_{fcc}$ is parallel to $[00.1]_{hcp}$.

TABLE I. Phonon energies of fcc $Co_{0.92}Fe_{0.08}$ at room temperature (in meV).

	[00ζ)			[ζζζ]			[ζζ0]		
ζ	T	L	ζ	T	L	ζ	T_1	T_2	L
0.15	6.5 ± 0.2		0.05	2.6 ± 0.1		0.05		3.1 ± 0.1	
0.20		12.0 ± 0.2	0.10	5.5 ± 0.1	10.8 ± 0.5	0.10		6.3 ± 0.1	8.5 ± 0.5
0.30	12.5 ± 0.2		0.20		23.0 ± 1	0.20	6.8 ± 0.1	12.2 ± 0.1	17.5 ± 0.2
0.40		22.0 ± 0.5	0.30	13.5 ± 0.1	31.8 ± 1	0.30			24.0 ± 1
0.50	18.7 ± 0.2		0.40	15.8 ± 1		0.40	13.4 ± 0.2	22.5 ± 0.5	
0.60		29.0 ± 0.5	0.50	16.0 ± 1	33.5 ± 2	0.50			31.8 ± 1
1.0	24.5 ± 1	32.0 ± 2				0.70			30.4 ± 1
						0.75	22.4 ± 1	32.0 ± 1	29.0 ± 1

tion number. No elastic scattering was observed at $q=\frac{1}{6}[\tau(111)]$ or $q=\frac{1}{3}[\tau(111)]$ which are special wave vectors for the fcc-to-hcp martensitic transition discussed above.

The phonon dispersion curves were measured at room temperature along the three principal symmetry directions: [001], [110], and [111]. Typical neutron groups are shown in Fig. 3 and the measured frequencies are given in Table I. The dispersion curves are plotted in Fig. 4. In the present experiment there was no observation of one-magnon scattering. It is easy to avoid confusion between phonon and magnon peaks since the energies of the magnons are much larger than the phonon energies for the q values studied.[6]

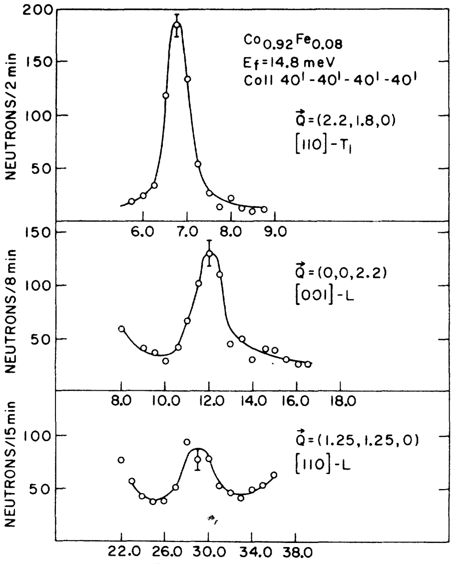

FIG. 3. Representative inelastic neutron spectra for several phonons in fcc $Co_{0.92}Fe_{0.08}$. The data were taken at room temperature with a fixed final neutron energy, $E_f = 14.8$ meV.

The peak positions of the spectra were used to generate a set of force constants by a least-squares fitting of our data to a Born–von Kármán expansion of the phonon frequencies.[7] The mass and lattice parameter used in these calculations were 58.7 amu and 3.55 Å, respectively. Axially symmetric and generalized force constants between an atom and its first, second, third, and fourth neighbors were tried. The fit obtained was

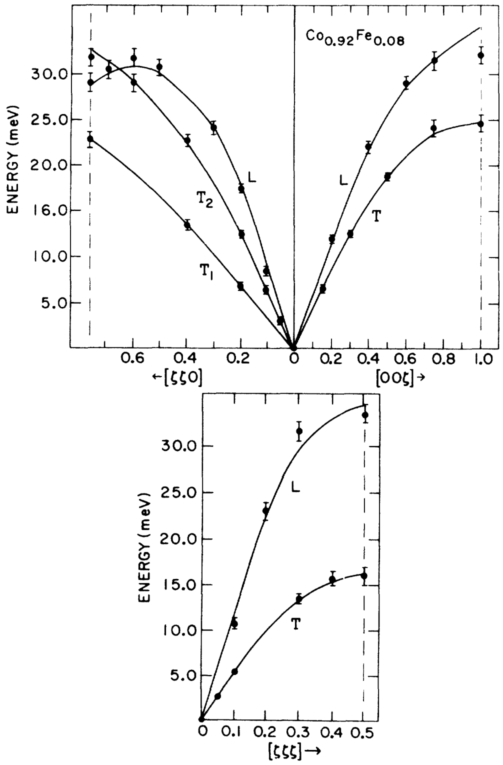

FIG. 4. Measured dispersion curve of fcc $Co_{0.92}Fe_{0.08}$ along three high-symmetry directions. The solid line is the calculated dispersion from the force constants given in Table II.

TABLE II. Interatomic force constants (in 10^4 dyne/cm) and elastic constants in (10^{12} dyne/cm^2) of $Co_{0.92}Fe_{0.08}$ at room temperature. These are axially symmetric four-neighbor forces. Symmetry $1xx = 1yy$; $1yz = 1xz = 0$; $2zz = 2yy$, $2yz = 2xz = 2xy = 0$; $3zz = 3yx$, $3xy = 3zx$; $4yy = 4xx$, $4yz = 4xz = 0$. The axial symmetry requires $1xy = 1xx - 1zz$; $3(3yz) = 3xx - 3yy$; $3(3zx) = 2(3xx) - 2(3yy)$; $4xy = 4xx - 4zz$. Also given are the values for nickel (Ref. 9).

Force constants	$Fe_{0.92}Co_{0.08}$	Ni
$1xx$	1.69 ± 0.07	1.77
$1zz$	-0.09 ± 0.08	-0.10
$1xy$	1.78 ± 0.09	1.87
$2xx$	-0.30 ± 0.06	0.115
$2yx$	0.05 ± 0.05	-0.01
$3xx$	0.04 ± 0.03	0.09
$3yy$	0.02 ± 0.03	0.02
$3yx$	0.007 ± 0.01	0.02
$3zx$	0.014 ± 0.02	0.05
$4xx$	0.09 ± 0.03	0.046
$4zz$	-0.03 ± 0.06	-0.015
$4xy$	0.12 ± 0.06	0.061
	Elastic constants	
C_{11}	2.21 ± 0.07	2.46
C_{12}	1.47 ± 0.09	1.50
C_{44}	1.24 ± 0.02	1.22

equally good for the generalized force constants and axially symmetric force constants. Table II presents the determined force constants for the axially symmetric model. Also given are the elastic constants obtained from the calculated force constants.

These force constants were then used to calculate a phonon density of states $g(\nu)$ with the aid of the program of Gilat and Raubenheimer[8] and is shown in Fig. 5. From this density of states the effective Debye temperature has also been calculated and is shown in Fig. 6.

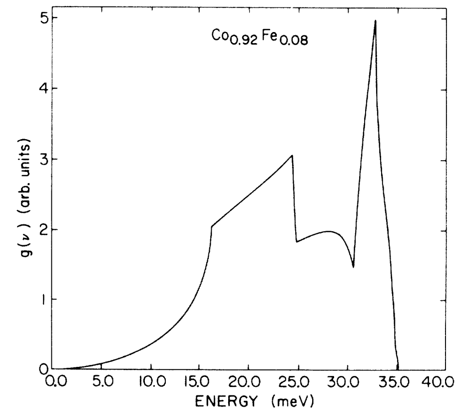

FIG. 5. Calculated density of states of fcc $Co_{0.92}Fe_{0.08}$ obtained from the measured force constants in Table II.

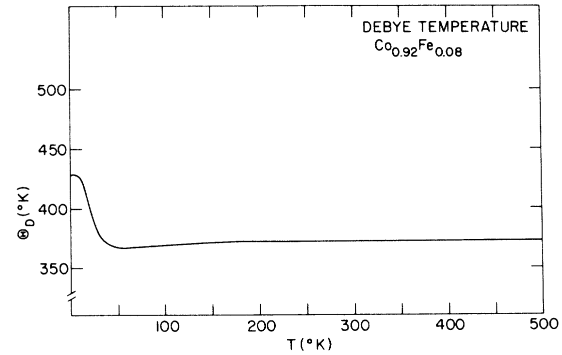

FIG. 6. Calculated temperature dependence of the Debye temperature for fcc $Co_{0.92}Fe_{0.08}$.

IV. DISCUSSION

It is useful to compare our results with those obtained for nickel, another fcc transition metal with one additional electron in the 3*d* shell. The force constants determined by Birgeneau *et al.*[9] for nickel are given in the second column of Table II as well as the determined elastic constants. The force constants between first neighbors are almost identical for fcc Co and fcc Ni. The elastic constants are also nearly identical. We can conclude that the fcc Ni and Co have almost identical lattice-dynamical properties. This is not so surprising since the lattice parameter and ionic radii of the two are almost identical as well as their masses. However, because of the additional *d* electron the magnetic properties of the two differ considerably.

To our knowledge, these are the only measurements of the lattice-dynamical properties of fcc Co. There have, however, been recent inelastic scattering measurements of single crystals of hcp Co.[10] As shown in Fig. 2 the [111] cubic direction is parallel to the $[00.1]_{hex}$ direction. The frequencies of the fcc and hcp crystals along these directions are nearly identical after allowing for the different Brillouin-zone sizes.

V. CONCLUSIONS

The lattice-dynamical properties of fcc cobalt with 8-at.% Fe have been measured. We believe that these properties are representative of pure fcc cobalt. We were unsuccessful in showing any premonitory effects of the fcc-hcp martensitic phase transition as anticipated from the Mössbauer results.[2] This is in retrospect not unexpected because we are so far above T_M. Two points are worth noting: (i) We must accept the existence of some kind of pretransitional fluctuation in order to explain the Mössbauer data, and (ii) the simple analysis in the Introduction should serve as a guide to future work and provide the positions in reciprocal space where we anticipate the fluctuations. Efforts are, therefore, still underway to find a suitable system to study in order to test the ideas of a lattice-dynamical triggering of the fcc-hcp martensitic phase transition.

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