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Elastic constants of some intermetallic compounds as determined by the rectangular parallelepiped resonance method*

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Abstract

The three elastic stiffness constants of various Ni-base intermetallic compounds Ni_3X with $L1_2$ structure have been determined by the rectangular parallelepiped resonance method. Two types of specimen chamber were constructed for low temperature (down to 90 K) and for high temperature (up to 1200 K) measurements. In order to reduce the amount of numerical calculation needed to derive the values of elastic constants from the resonance spectrum, we have developed a systematic and efficient method of analysis, which is valid for crystals of cubic symmetry.

1. Introduction

In recent years, the investigation of intermetallic compounds has been one of the subjects of intensive research activity. While extensive investigations have been performed on the plastic properties of various intermetallic compounds, the investigation of elastic properties has been rather limited. The knowledge of single-crystal elastic constants is the essential basis for the real understanding of the elasticity of the relevant material.

Measurements of single-crystal elastic constants have usually been performed by measuring the velocity of elastic waves propagating in a material; the specimen size required is typically about a 10 mm length. Growth of single crystals of intermetallic compounds with such a size is not always easy. An alternative method is the rectangular parallelepiped resonance (RPR) method which allows the use of smaller specimens. The theoretical basis of the method has been given by Demarest [1], who derived the resonance frequencies of a vibrating specimen with cubic symmetry and shape. Ohno has extended the theory for a rectangular parallelepiped specimen of orthorhombic symmetry [2], and Ohno *et al.* dealt with trigonal symmetry [3]. Extensive efforts have been made by Migliori *et al.* to obtain reliable values of elastic constants by the RPR method [4]. Although there have been several reports of elastic constants determined by the RPR method, most of them are on materials for which the elastic constants were previously determined by some other methods. This is because of the difficulty in deducing the values of the elastic constants from a measured resonance spectrum. It is straightforward to calculate the resonance frequencies if the elastic constants are known, but the reverse procedure is not at all simple. Until now the determination of the elastic constants from a given resonance spectrum has therefore been done by trial and error, which is inevitably very time consuming. A systematic method of data analysis is badly needed.

The present authors have developed such a systematic method valid for specimens with cubic symmetry [5]. The method has been applied to measure elastic constants of the intermetallic compounds Co_3Ti and CoTi [6], and a series of Ni-based $L1_2$-type compounds [7], at room temperature. High temperature measurements were also made for some compounds to reveal the anomalous temperature dependence of the elastic anisotropy for Ni_3Ge [8]. The aim of this paper is to review these investigations performed by the present authors.

2. Experimental apparatus

The system for measuring the resonance spectrum is shown in Fig. 1. A rectangular parallelepiped specimen is held at the body diagonal corners between the two piezoelectric transducers. A sinusoidal signal from the synthesized function generator is applied to one of the transducers. If the specimen is in resonance with the applied frequency, the mechanical vibration is transmitted to the other transducer. The output signal is amplified, rectified and fed to the analogue–digital converter, and then the digitized data are transferred

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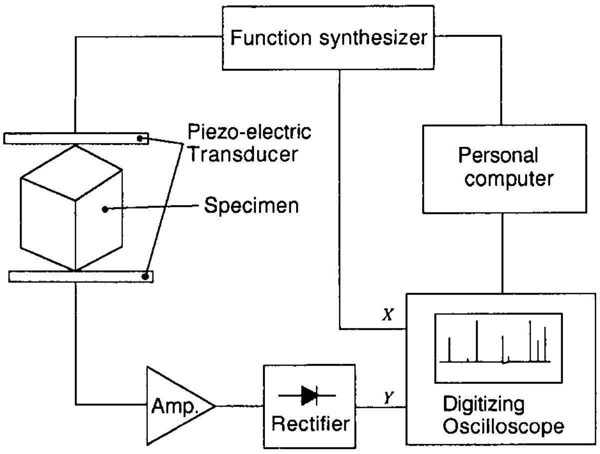

Fig. 1. Schematic diagram showing the RPR method.

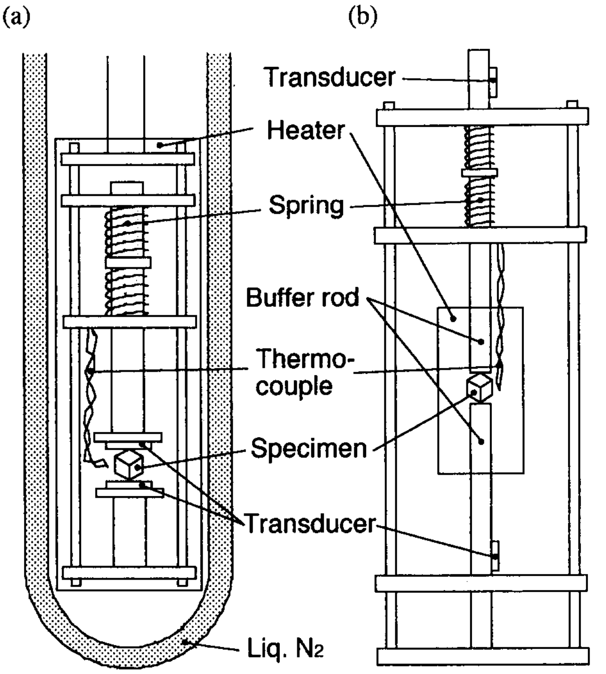

Fig. 2. Specimen chambers for (a) low and (b) high temperature measurements.

to the personal computer. By sweeping the excitation frequency, a resonance spectrum is obtained for the specimen in a certain frequency range, which is usually from 100 to 1500 kHz. Measurements below and above room temperature are made in separate specimen chambers, with a common control and data acquisition system.

The specimen chamber for low temperatures is schematically illustrated in Fig. 2(a); the chamber is first evacuated and is filled with helium gas during measurements. The specimen temperature is changed by a computer-controlled heater. The accuracy of the specimen temperature is about 0.3 K in the temperature range from 77 K to room temperature.

Measurements at high temperatures but below the piezoelectric Curie temperature of the relevant transducer material can in principle be made by using the low temperature chamber in Fig. 2(a), although the deterioration of the transducer itself and of the electrode connection on exposure to high temperatures in vacuum might considerably reduce the range of temperatures for successful measurements. In order to avoid such a difficulty, we constructed a high temperature chamber, adopting the design produced by Goto and Anderson [9], as schematically shown in Fig. 2(b). The specimen is held by the two alumina buffer rods about 5 mm in diameter and 170 mm in length, which guide the vibration from or to the piezoelectric transducers. The buffer rods are supported by collimators with a spring to hold the specimen gently so as to accommodate thermal expansion. Measurements are made in vacuum so as to avoid the oxidation of specimens.

3. Method of analysis

For a rectangular parallelepiped specimen of known dimensions and density, a set of resonance frequencies can be calculated if the values of elastic constants are given; the prescription has been given, *e.g.* by Demarest [1]. There is no straightforward way, however, for the reverse process of deriving the value of elastic constants from a given resonance spectrum. Therefore the analysis has to be made essentially by trial and error; a set of frequencies calculated for an assumed set of elastic constants is compared with a set of observed frequencies, and the procedure is repeated until a satisfactory agreement is obtained. In order to carry out this procedure efficiently, we developed a method valid for crystals of cubic symmetry, as described below.

The elasticity of a cubic crystal is specified by the three independent elastic constants c_{11}, c_{12} and c_{44}. In analysing the resonance spectrum, it is convenient to deal with the following set of three elastic constants or parameters: the shear modulus of the {100} planes c_{44}; Poisson's ratio along the ⟨100⟩ direction ν; and the anisotropy factor A, or the ratio of the shear modulus on {100} planes to that on {110} planes. The latter two parameters are defined by

$$\nu=\frac{c_{12}}{c_{11}+c_{12}} \tag{1}$$

$$A=\frac{2c_{44}}{c_{11}-c_{12}} \tag{2}$$

Note that c_{44} can be regarded as a scaling factor of the elastic constants which determines the absolute magnitude of the resonance frequencies, while the two parameters ν and A define the structure of the resonance spectrum.

From the lattice stability condition, the elastic constants must satisfy the following three inequalities for the cubic system:

$$c_{11}+2|c_{12}|>0 \tag{3}$$

$$c_{11}-c_{12}>0 \tag{4}$$

$$c_{44}>0 \tag{5}$$

In terms of ν and A, these conditions can be rewritten as

$$-1<\nu<\frac{1}{2} \tag{6}$$

$$A>0 \tag{7}$$

No real material is known to have a negative value of ν. Thus, eqn. (6) can be replaced with

$$0<\nu<\frac{1}{2} \tag{8}$$

In Fig. 3 are plotted the values of A *vs.* ν for various materials with cubic symmetry: b.c.c., f.c.c., or the diamond cubic structures [10]. Note that the data points lie near the full curve which represents the Cauchy relation $c_{12}/c_{44}=1$, or $A-2\nu=2A\nu$. The values of A for most materials are smaller than 10, although some b.c.c. metals have larger values. Thus, in the search for the values of the elastic constants, we now have a very good map indicating the areas to be examined carefully. The greater advantage of dealing with the set c_{44}, A and ν rather than with c_{44}, c_{12} and c_{11} is evident; for the latter, it is difficult to predict plausible ranges of values for c_{12} and c_{11}.

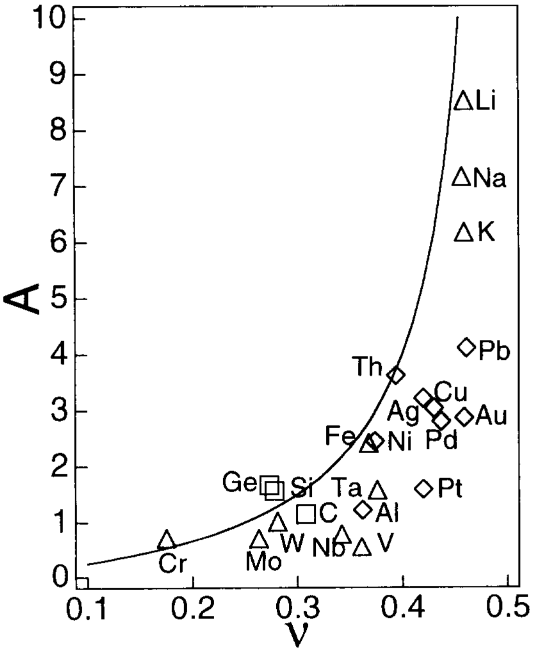

Fig. 3. Values of the anisotropy factor A and Poisson's ratio ν for monatomic solids with cubic symmetry: ◇, f.c.c.; △, b.c.c.; □, diamond cubic; ——, Cauchy relation $c_{12}/c_{44}=1$ or $A-2\nu=2A\nu$.

Preceding the analysis of a measured spectrum, a set of resonance frequencies are calculated for various combinations of ν and A and stored in a computer. The analysis is made by comparing the measured set of resonance frequencies with the stored ones. The results are refined by the method of least squares; the details were described in a previous paper [5].

4. Results and discussion

Single-crystal elastic constants were determined at room temperature for a series of Ni-base $L1_2$ compounds Ni_3X with X = Mn, Fe, Al, Ga, Ge and Si [7]. Table 1 lists the composition, dimensions and density of specimens used for measurements. The elastic constants are listed in Table 2, together with the data for Ni_3Al [11] and Ni [12]. Here, c' is the shear modulus of $(110)[1\bar{1}0]$ type: $c'=(c_{11}-c_{12})/2$. Figure 4 shows for Ni_3Ge the temperature dependence of the elastic moduli c_{44} and c' and anisotropy factor A [8].

In the present method of analysis, the observed set of frequencies are compared in turn with the precalculated and stored sets of frequencies for various combinations of Poisson's ratio ν and the elastic anisotropy A. As an example, the experimental resonance spectrum and several sets of calculated frequencies are shown

TABLE 1. Specimens used for the measurements of the elastic constants

Specimen	Composition (at.%)	Edge length (mm)			Density ($\times 10^3$ kg m^{-3})
		x	y	z	
Ni_3Mn	23.5Mn	3.613	3.743	3.889	8.12
Ni_3Fe	25.0Fe	4.118	4.091	4.453	8.52
Ni_3(Al, Ti)	15Al–9Ti	2.825	2.794	2.740	7.50
Ni_3Ga	24.7Ga	2.483	3.055	2.246	8.34
Ni_3Ge	25.0Ge	4.639	4.638	4.718	8.92
Ni_3(Si, Ti)	13Si–9Ti	4.754	4.621	4.718	7.91

TABLE 2. Elastic constants (GPa) of the $L1_2$ intermetallic compounds [7][a]

	c_{11}	c_{12}	c_{44}	c'	ν	A
Ni_3Mn (order)	244.5	165.3	145.0	39.6	0.403	2.903
Ni_3Mn (disorder)	236.9	161.9	110.6	37.4	0.406	2.960
Ni_3Fe (order)	250.8	153.8	123.0	48.5	0.380	2.535
Ni_3Fe (disorder)	236.1	148.5	119.9	43.8	0.386	2.738
Ni_3Al	221.0	146.0	124.0	37.5	0.398	3.307
Ni_3(Al, Ti)	259.8	176.9	124.3	41.5	0.405	2.997
Ni_3Ga	191.1	123.2	107.5	33.9	0.392	3.165
Ni_3Ge	263.0	143.0	103.0	60.0	0.352	1.717
Ni_3(Si, Ti)	255.0	169.0	120.0	43.0	0.399	2.791
Ni	250.8	150.0	123.5	50.4	0.374	2.450

[a] The values for Ni_3Al and Ni are taken from ref. 11 and ref. 12 respectively.

in Fig. 5. In the analysis, only numerical values of resonance frequencies are used for the determination of elastic constants; the observed spectrum (Fig. 5(a)) is represented by the line diagram of Fig. 5(b), which should be compared in turn with those of calculated spectra in Figs. 5(c)–5(f). After finding a candidate combination, in this case Fig. 5(c), the final refinement is made by the least-squares method, *i.e.* by minimizing the quantity

$$S=\sum_i\left(\frac{f_i^{\mathrm{cal}}-f_i^{\mathrm{obs}}}{f_i^{\mathrm{cal}}}\right)^2 \tag{9}$$

where f_i^{cal} and f_i^{obs} are calculated and observed resonance frequencies. Finally, the elastic constants c_{11}, c_{12} and c_{44} can be obtained from eqns. (1) and (2).

In practice, account must be taken of the fact that some modes of oscillation are difficult to excite or very weakly excited and might be absent in the measured resonance spectrum; f_i^{obs} corresponding to the calculated frequency f_i^{cal} for a certain i might not be measured.

The intrinsic difficulty involved in the analysis is lack of a knowledge of the type of vibrational mode for each resonance frequency of the observed spectrum. If the mode of vibration can be experimentally determined for each peak in the resonance spectrum, the derivation of the elastic constant can be performed more reliably. Such efforts are being made in our laboratory.

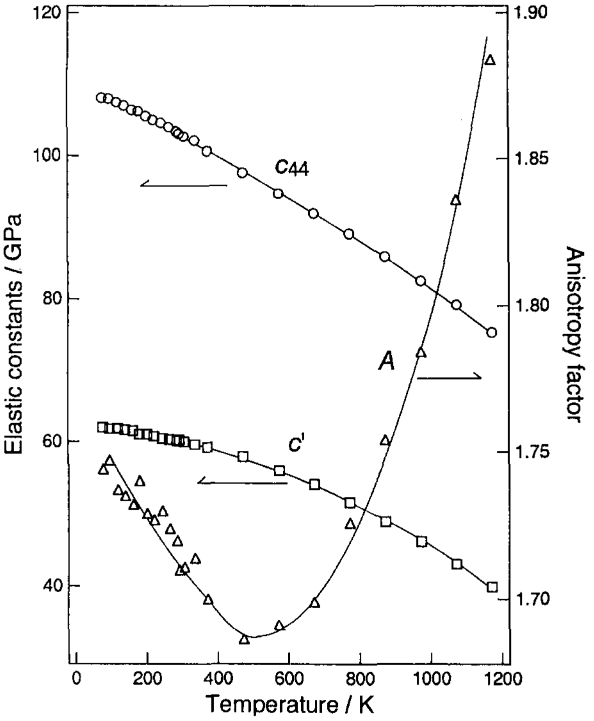

Fig. 4. Temperature dependence of the elastic moduli c_{44} and c' and anisotropy factor A of Ni_3Ge.

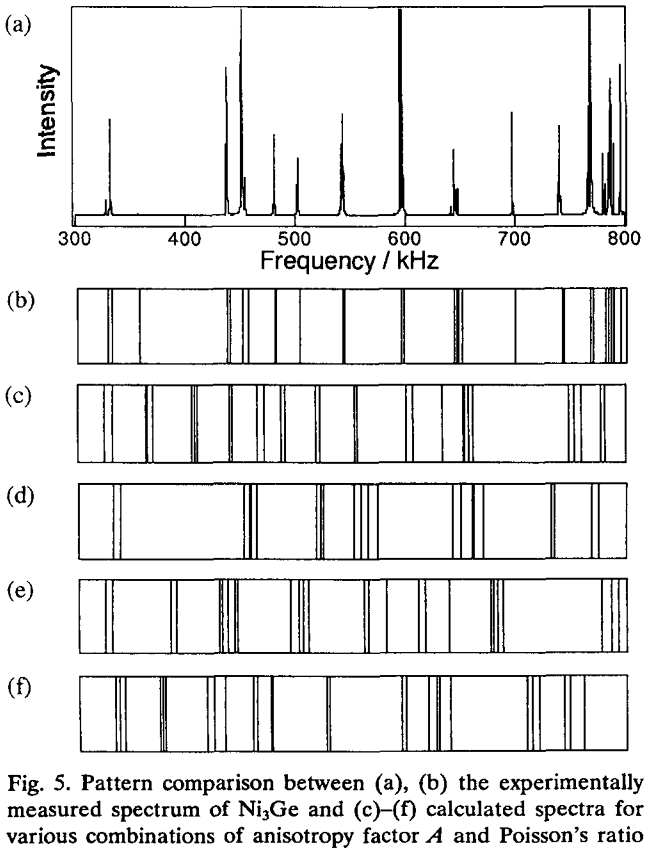

Fig. 5. Pattern comparison between (a), (b) the experimentally measured spectrum of Ni_3Ge and (c)–(f) calculated spectra for various combinations of anisotropy factor A and Poisson's ratio ν: (c) $A=1.6$, $\nu=0.36$; (d) $A=1.0$, $\nu=0.36$; (e) $A=1.4$, $\nu=0.39$; (f) $A=2.0$, $\nu=0.30$.

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