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The Heusler structure of Au_2MnAl . By D. P. MORRIS, C. D. PRICE and J. L. HUGHES, *Department of Physics, University College of North Wales, Bangor, Wales*

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The Heusler structure is body-centred cubic with a face-centred superlattice, and may be thought of as four interpenetrating face-centred cubic lattices A , B , C , and D , of which A and C are identical. In the well-known ferromagnetic Heusler alloys Cu_2MnX , Cu atoms lie on lattices A and C , Mn atoms on B , and X atoms (which may be Al, In, or Sn) on D . The structure factor formula (Bradley & Rogers, 1934) takes the following forms: (1) main lines, $Q^2 (= h^2 + k^2 + l^2) = 8, 16, 24, \dots$, $F = f_A + f_B + f_C + f_D$; (2) even superlattice lines, $Q^2 = 4, 12, 20, \dots$, $F = (f_A + f_C) - (f_B + f_D)$; (3) odd superlattice lines, $Q^2 = 3, 11, 19, \dots$, $F = \{(f_A - f_C)^2 + (f_B - f_D)^2\}^{1/2}$; where f_A, f_B, \dots are the scattering factors of the atoms on the A, B, \dots lattices. The structure is distinguishable from the $B2$ or CsCl type, in which lattices B and D are also identical, by reflexions of type (3) if there is a sufficiently large difference in the scattering factors of the atoms on B and D .

In an earlier attempt to discover gold-based Heusler alloys (Morris, Preston & Williams, 1959) this difference proved too small to allow these reflexions to be detected with certainty by conventional X-ray film and microphotometer techniques, although the ferromagnetism exhibited by the alloy at low temperatures suggested that the Heusler structure existed. This has now been confirmed both by neutron diffraction (Bacon, 1962*a*) for which the scattering factors are more suitable, and by our own re-examination with an X-ray diffractometer.

Powder samples annealed at 700 °C for 24 hours or more were examined after different rates of cooling. After quenching of the samples in iced water no reflexions other than the even superlattice and main lines were definitely detected, but after they had been cooled to room temperature over a period of 6 hours two small peaks appeared which were identified as the 111 and 311 reflexions of a Heusler structure of lattice parameter 6.358 Å. A slower cooling rate (over about 3 days) produced additional lines which were indexed as belonging to a second cubic structure of lattice parameter 5.993 Å. This is presumably the Al_2Au phase (Pearson, 1958), so that the equilibrium structure of Au_2MnAl at lower temperatures is two-phase. The results show that the ordered arrangement of the Mn and Al atoms on the B and D lattices is at least partially destroyed on raising

the temperature but the X-ray intensities are too small to make any accurate quantitative measurements on the degree of order. The latter however has a marked effect on the magnetic properties, the saturation intensity (extrapolated to infinite field and absolute zero) increasing from about 24 e.m.u.g⁻¹ for a quenched sample to about 55 e.m.u.g⁻¹ for a slow-cooled sample. The Curie point of the latter is -53 °C. The detailed magnetic measurements and the thermal expansion of Au_2MnAl and $\text{Au}_2\text{Mn}_{2-x}\text{Al}_x$ ($0 < x < 1$) will be reported elsewhere.

A comparison of the crystal structures and magnetic properties of AuMn and Au_2MnAl is also of interest. AuMn has a CsCl type of structure and is antiferromagnetic, but the observed magnetic structure (Bacon, 1962*b*) is not that in which nearest neighbours in the simple cubic lattice of Mn atoms are antiferromagnetically aligned. Instead there appears to be a strong antiferromagnetic exchange interaction between the pairs of Mn atoms situated at the ends of a body diagonal. In the Heusler structure of Au_2MnAl every alternate Mn atom along cube edges in AuMn is replaced by Al, so that along $\langle 111 \rangle$ directions the sequence of atoms is changed from Mn-Au-Mn-Au-Mn to Mn-Au-Al-Au-Mn. We suggest that the antiferromagnetic coupling in AuMn is due to indirect exchange interaction between Mn atoms via an intervening Au atom. This has been removed in Au_2MnAl and the alloy is ferromagnetic.

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References

- BACON, G. E. (1962*a*). Private communication.
 BACON, G. E. (1962*b*). *Proc. Phys. Soc.* **79**, 938.
 BRADLEY, A. J. & RODGERS, J. W. (1934). *Proc. Roy. Soc. A*, **144**, 340.
 MORRIS, D. P., PRESTON, R. R. & WILLIAMS, I. (1959). *Proc. Phys. Soc.* **73**, 520.
 PEARSON, W. B. (1958). *Handbook of Lattice Spacings and Structure of Metals*, p. 315. London: Pergamon Press.

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Fourth-order elastic coefficients in crystals. By T. S. G. KRISHNAMURTY, *Andhra University, Waltair, India*

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Starting from Murnaghan's theory (1937) of finite strain, Birch (1947) considered the theory of finite elastic strain for a medium of cubic symmetry in which the expression for free energy contains third-order strain components. Introducing the concept of effective elastic constants,

Chelam (1961) has recently studied the effect of large stresses on elastic solids, and the results he obtained by taking the second-order and third-order strain components in the strain-energy expression are not in complete agreement with the experimental results. To obtain

qualitative and quantitative agreement between theory and experiment, Chelam suggested that one has to include the fourth-order strain components also in the strain-energy function.

Physical properties of substances generally arise out of, and represent the relation between, two quantities each of which may be a scalar, or a vector or a symmetric tensor of second order, *etc.* For instance, the density of a substance is the relation between two scalars, whereas the dielectric constant represents the relation between two vectors. Similarly elasticity arises out of the relation between the applied-stress tensor and the resulting strain tensor. Fourth-order elasticity is the relation between a symmetric stress tensor and the cube of a symmetric strain tensor with the additional condition that the coefficients C_{ijkl} satisfy the relations $C_{ijkl} = C_{jikl} = C_{ijlk} = C_{iklj}$ *etc.*, ($i, j, k, l = 1, 2, 3, 4, 5, 6$). Under this condition, one can see that the maximum number of fourth-order elastic coefficients is 126, which is the actual number for a triclinic crystal.

Using the following expressions

$$\left. \begin{aligned} \alpha_{xx} &\rightarrow \alpha_{xx} \cos^2 \varphi + \alpha_{yy} \sin^2 \varphi + 2\alpha_{xy} \cos \varphi \sin \varphi \\ \alpha_{yy} &\rightarrow \alpha_{xx} \sin^2 \varphi + \alpha_{yy} \cos^2 \varphi - 2\alpha_{xy} \sin \varphi \cos \varphi \\ \alpha_{zz} &\rightarrow \alpha_{zz} \\ \alpha_{yz} &\rightarrow \pm \alpha_{yz} \cos \varphi \mp \alpha_{zx} \sin \varphi \\ \alpha_{zx} &\rightarrow \pm \alpha_{yz} \sin \varphi \pm \alpha_{zx} \cos \varphi \\ \alpha_{xy} &\rightarrow (-\alpha_{xx} + \alpha_{yy}) \sin \varphi \cos \varphi + \alpha_{xy} (\cos^2 \varphi - \sin^2 \varphi), \end{aligned} \right\} (1)$$

for the transformation of the components $\alpha_{xx}, \dots, \alpha_{xy}$ of a second-order symmetrical tensor under a rotation or a rotation-reflection through an angle φ about the z axis, the terms contributed by each of these 126 constants to the character (Bhagavantam & Suryanarayana, 1949) are calculated. The character so obtained from these 126 coefficients is given by

$$\left. \begin{aligned} \chi'_i(R) &= 256 \cos^8 \varphi \pm 128 \cos^7 \varphi - 320 \cos^6 \varphi \\ &\mp 96 \cos^5 \varphi + 160 \cos^4 \varphi \pm 24 \cos^3 \varphi \\ &- 28 \cos^2 \varphi + 2, \end{aligned} \right\} (2)$$

the upper sign referring to pure rotations and the lower sign to rotation-reflections. Applying the general formula (Bhagavantam & Venkatarayudu, 1951)

$$n_i = \frac{1}{N} \sum_j h_j \chi'_j(R) \chi_i(R), \quad (3)$$

the values of n_i appropriate to the total symmetric irreducible representation, which is characterized by the fact that $\chi_i(R) = 1$ for all R , are found in respect of the 32 crystal classes and are given hereunder:

$$\begin{aligned} E, C_i: &126; C_s, C_2, C_{2h}: 70; C_{2v}, D_2, D_{2h}: 42; C_4, S_4, C_{4h}: \\ &36; C_{4v}, S_{4v}, D_4, D_{4h}: 25; C_3, S_6: 42; C_{3v}, D_3, D_{3d}: 28; \\ &C_{3h}, C_6, C_{6h}: 24; D_{3h}, C_{6v}, D_6, D_{6h}: 19; T, T_h: 14; \\ &T_d, O, O_h: 11. \end{aligned}$$

We again observe (Bhagavantam & Suryanarayana, 1947) that the five point groups coming under the cubic system can be divided into two classes so far as the fourth-order elastic coefficients are concerned.

The number of fourth-order elastic coefficients for a perfect isotropic solid can be obtained from the following formula (Venkatarayudu & Krishnamurty, 1952):

$$n_i = \frac{1}{2\pi} \int_0^{2\pi} (\chi'_+ \chi_- + \chi'_- \chi_+) d\varphi, \dots \quad (4)$$

where χ'_\pm is the same as $\chi'_j(R)$ given by (2), and $\chi_\pm = 1 \pm \cos \varphi$. Substituting the values of χ'_\pm and χ_\pm in (4), we obtain the value 4 for n_i , and this represents the number of independent fourth-order elastic coefficients of an isotropic solid, which are described below.

The 11 independent fourth-order elastic coefficients coming under the O_h point group of the cubic system may be described by the following relations:

$$\left. \begin{aligned} C_{1111} &= C_{2222} = C_{3333}, \\ C_{4444} &= C_{5555} = C_{6666}, \\ C_{1112} &= C_{1113} = C_{2223} = C_{3331} = C_{3332} = C_{2221}, \\ C_{1123} &= C_{2213} = C_{3312}, \\ C_{4412} &= C_{5523} = C_{6613} = C_{4413} = C_{5512} = C_{6623}, \\ C_{4423} &= C_{5513} = C_{6612}, \\ C_{1456} &= C_{2456} = C_{3456}, \\ C_{1122} &= C_{2233} = C_{1133}, \\ C_{1144} &= C_{2255} = C_{3366}, \\ C_{1155} &= C_{1166} = C_{2244} = C_{3355} = C_{2266} = C_{3344}, \\ C_{4455} &= C_{4466} = C_{5566}. \end{aligned} \right\} (5)$$

In the case of isotropic solids, there are seven further relations among these eleven, namely:

$$\left. \begin{aligned} 4C_{1111} &= C_{1112} + C_{1155}, \\ 6C_{1111} &= C_{6666} + C_{1122} + C_{2344}, \\ 3C_{1112} &= C_{1244} + C_{1123}, \\ 2C_{1122} &= C_{1123} + C_{1144}, \\ 3C_{1155} &= C_{1244} + C_{1456} + C_{1144} + C_{4455}, \\ 2C_{6666} &= C_{4455}, \\ 2C_{1244} + C_{1456} &= 2C_{2344}. \end{aligned} \right\} (6)$$

This again confirms our earlier conclusion that the number of independent fourth-order elastic coefficients of an isotropic solid reduces itself to 4 only.

One may easily see that the number of n th order elastic coefficients, symmetric in all the n suffixes, which belong to the O_h point group of the cubic system, will be $n^2 - 2n + 3$ ($n \geq 2$), whereas for an isotropic solid the corresponding number would be n only.

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References

- BHAGAVANTAM, S. & SURYANARAYANA, D. (1947). *Nature, Lond.* **160**, 750.
 BHAGAVANTAM, S. & SURYANARAYANA, D. (1949). *Acta Cryst.* **2**, 21.
 BHAGAVANTAM, S. & VENKATARAYUDU, T. (1951). *Theory of Groups and its Applications to Physical Problems*, p. 207. Andhra University.
 BIRCH, F. (1947). *Phys. Rev.* **71**, 809.
 CHELAM, E. V. (1961). Thesis submitted to the Indian Institute of Science, Bangalore.
 MURNAGHAN, F. D. (1937). *Amer. J. Math.* **49**, 235.
 VENKATARAYUDU, T. & KRISHNAMURTY, T. S. G. (1952). *Acta Cryst.* **5**, 287.