same order as the expected density of dislocations in zinc single crystals grown under similar conditions.

(2) Besides individual etch pits, linear arrays of pits suggestive of small angle boundaries have been observed.

(3) The formation of a flat-bottomed pit, indicating that the dislocation has moved during etching, is noted.

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Optical Activity in a Non-Enantiomorphous Crystal of Class $\bar{4}$: $CdGa_2S_4$

BY M. V. HOBDEN
Royal Radar Establishment, Malvern, Worcestershire, England

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Optical activity has been observed for the first time in a crystal of the non-enantiomorphous class $\bar{4}$. $CdGa_2S_4$ is optically isotropic at 4872 Å (20 °C) and this allows observation of optical rotation for propagation in directions away from the *c* axis. The magnitude of the optical rotatory power is 17·3 deg.mm^{-1} along ⟨100⟩ and 11·6 deg.mm^{-1} along ⟨110⟩. The form of the optical rotatory power for general directions in the (001) plane has the predicted symmetry, showing positive and negative lobes. The refractive indices and birefringence are temperature-dependent and the point of isotropy shifts from 4825 Å at 0 °C to 5780 Å at 400 °C.

Introduction

To a first approximation, light is propagated in crystalline media by two transverse linearly polarized modes of propagation. However, in media of certain symmetries a small perturbation to these linear modes can arise when the dimensions of the basic structure unit are not negligible compared with the wavelength of the light. In general the two modes of propagation are then elliptically polarized with slightly modified phase velocities. Optical phenomena due to these small perturbations are generically termed optical activity.

A phenomenological theory of optical activity, based upon a gyration tensor (Nye, 1964) has explained the symmetry properties of optical activity in the various crystal classes with success. It can be shown that optical activity is allowed by symmetry in only 15 of the 32 crystal classes. These are the 11 enantiomorphous classes 1, 2, 222, 4, 422, 3, 32, 6, 622, 432 and 23 and the four non-enantiomorphous classes *m*, *mm*2, $\bar{4}$ and $\bar{4}2m$. It has recently been shown for the first time that optical activity can exist in a non-enantiomorphous crystal (Hobden, 1967, 1968*a*); it was found that $AgGaS_2$ (class $\bar{4}2m$) was accidently optically isotropic at 4974 Å and this allowed the optical rotatory power to be measured in directions away from the *c* axis.

$CdGa_2S_4$ (class $\bar{4}$) has a similar isotropy point and also exhibits optical activity (Hobden, 1968*b*). This phenomenon has been examined in more detail and the dependence of the optical rotatory power on direction of propagation and also crystal temperature is now reported.

The structure of $CdGa_2S_4$

It has been shown by Hahn, Frank, Klingler, Storger & Storger (1955), using powder diffraction techniques, that $CdGa_2S_4$ has spatial symmetry $I\bar{4}$ with cadmium on the (*a*) sites, gallium on the (*b*) and (*c*) sites, and sulphur on the (*g*) sites ($x=0·27$, $y=0·26$, $z=0·14$). It is therefore a uniaxial, acentric non-enantiomorphous crystal of class $\bar{4}$.

The compound was prepared by fusion of CdS and Ga_2S_3, each of which was prepared from high purity elements. Slow crystallization by the Stockbarger technique (m.p. ~ 1050 °C) in sealed quartz tubes produced a polycrystalline matrix from which single-crystal pieces up to 8 mm in diameter were cut. Polished plates prepared from these crystals were examined with the polarizing microscope and found to be yellow in colour, uniaxial, and of good optical quality. These plates gave a positive response to the Giebe–Scheibe test for piezoelectricity thereby confirming acentricity. X-ray powder patterns agreed closely with a computed pattern based upon the reported structure, though our unit-cell dimensions were $a=5.54(6)$ and $c=10·16$ Å ($K\alpha_1=1·5405$ Å) compared with $a=5·57(6)$ and $c=10·08$ Å derived from the published data mentioned above. The measured density of the polycrystalline matrix, which appeared to have some small voids, was 3·93 g.cm^{-3} compared with the theoretical 4·037 g.cm^{-3}.

The refractive indices of $CdGa_2S_4$

From a single crystal a 14° 59′ prism was prepared with faces approximately 6mm × 6mm, the *c* axis being parallel to the roof edge. The refractive indices were measured at 20 °C by the minimum deviation method using a spectrometer and spectral emission lines. The data are shown in Fig. 1 and Table 1. It can be seen that $CdGa_2S_4$ has a weak positive birefringence ($n_e - n_o$) at the blue end of the spectrum but a weak negative birefringence at the red end; between 4800 and 4900 Å there is evidently a wavelength at which the birefringence is zero and the crystal is optically isotropic.

Table 1. *The refractive indices of* $CdGa_2S_4$ *at* 20 °C

λ_0	n_e	n_o	$n_e - n_o$
7065 Å	2·374	2·378	−0·004
6678	2·385	2·389	−0·004
6402	2·395	2·398	−0·003
6143	2·405	2·408	−0·003
5876	2·418	2·421	−0·003
5780	2·423	2·425	−0·002
5570	2·435	2·437	−0·002
5461	2·442	2·444	−0·002
5341	2·451	2·452	−0·001
5016	2·479	2·480	−0·001
4922	2·488	2·488	0·000
4713	2·512	2·511	+0·001
4471	2·547	2·545	+0·002
4358	2·568	2·565	+0·003

The birefringence of $CdGa_2S_4$

More accurate measurements of birefringence were made with polished plates cut parallel to the *c* axis. These were placed between a crossed polarizer and analyser, in the 45° position. With white light illumination and a calibrated direct vision spectrometer the position of the dark fringes in the transmitted spectrum could be measured to ± 3 Å. The dark fringes occur when

$$(n_e - n_o)l = N\lambda_0 \qquad (1)$$

where l is the length of the crystal, λ_0 is the free-space wavelength and N is a small integer. If N can be determined the value of ($n_e - n_o$) can be found at each of these dark fringe positions.

With a crystal plate 1·837 mm thick, twenty-four dark fringes were observed and measured. By comparing these fringes with the crude birefringence data in Table 1 it was possible to identify the fringe of zero birefringence ($N = 0$) at 4872 Å. The absolute birefringence at the other dark fringe positions was then calculated from equation (1) to about $\pm 3 \times 10^{-5}$. These data are shown in Fig. 2 together with the less accurate birefringence data from Table 1 for comparison.

Optical rotation in $CdGa_2S_4$

Optical activity is a weak effect compared with birefringence and in general optical activity can only be observed when the birefringence is very small or zero.

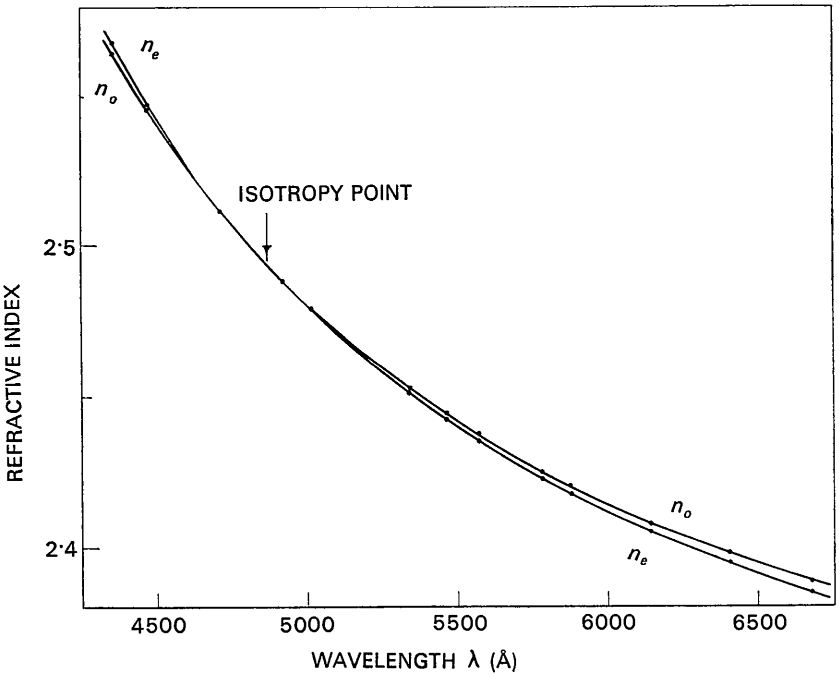

Fig. 1. The refractive indices of $CdGa_2S_4$ at 20 °C showing that there is a wavelength at which the birefringence is zero.

By symmetry there can be no optical rotation along a $\bar{4}$ axis; in other directions crystals of this symmetry are in general birefringent. For this reason crystals of class $\bar{4}$ do not exhibit observable optical activity unless some special circumstances arise. In this case the accidental optical isotropy $CdGa_2S_4$ at 4872 Å allows measure-

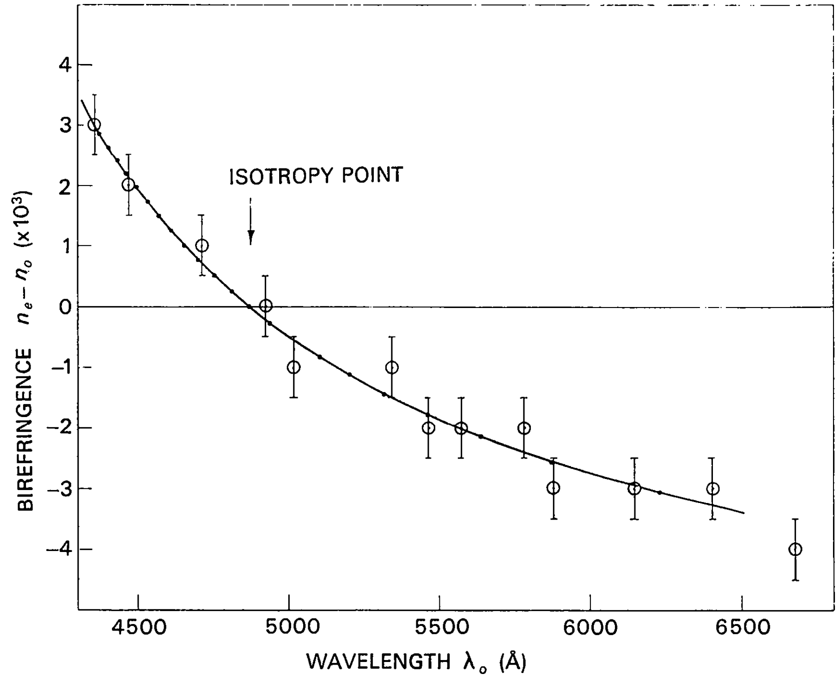

Fig. 2. The birefringence of $CdGa_2S_4$ at 20 °C derived from measurements of transmission fringes showing the isotropy point at 4872 Å. Also shown are the data derived from refractive index measurements.

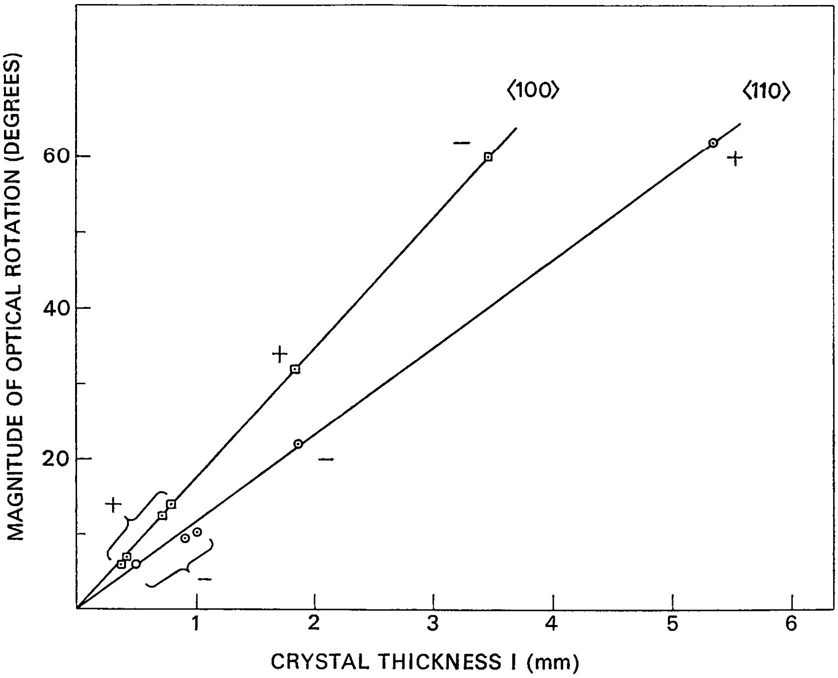

Fig. 3. The magnitude and sign of the optical rotation for various directions of propagation in crystals of different thickness.

ments of the rotation of the plane of polarization to be made for all directions of propagation in the crystal.

In crystals of $\bar{4}$ symmetry the optical rotatory power, in the absence of birefringence is

$$\varrho = \pm[(g_{11}(l_1^2 - l_1^2) + 2g_{12}\, l_1 l_2](\pi/\lambda_0 n) \qquad (2)$$

radians per unit length, where g_{11} and g_{12} are the independent non-zero elements of the gyration tensor, λ_0 is the free-space wavelength, and n is the refractive index. The propagation direction has direction cosines l_1, l_2 with respect to the ⟨100⟩ axes; the ± sign indicates that there is a change of sign of the rotation depending upon the choice of ⟨100⟩ as reference axes. It can be seen from this equation that there should be no optical rotation along the *c* axis. In ⟨100⟩ directions the optical rotatory power is $\pm g_{11}{}^{\pi}/\lambda_0 n$ and in ⟨110⟩ directions it is $\pm g_{12}{}^{\pi}/\lambda_0 n$.

A single crystal was oriented by *X*-ray techniques and cut to provide a variety of small parallel sided pieces of various thicknesses with normals along [100] [010] and [110] [1$\bar{1}$0] directions. Our labels [100] and [010] are arbitrary because there are no conventions in this crystal class to distinguish [100] from [010]. With light at 4872 Å the rotation of the plane of polarization was measured for various thickness of crystal. From these measurements it could be shown, without ambiguity, that the magnitude of the effect along [100] and [010] directions was 17·3 deg. mm^{-1} but of the opposite sign. For [110] and [1$\bar{1}$0] directions the rotation was 11·6 deg. mm^{-1} but of opposite sign. The data are shown in Fig. 3 (to assist interpretation the magnitude of the rotation is shown; it is to be understood that the sense of the rotation shown was of the opposite hand for [100] and [010] and for [110] and [1$\bar{1}$0] directions). This is in agreement with equation (2) with $g_{11} = 1{\cdot}17 \times 10^{-4}$, $g_{12} = 0{\cdot}78 \times 10^{-4}$, $n = 2{\cdot}494$ and $\lambda_0 =$ 4872 Å. Other crystal plates were prepared with normals in general directions in the (001) plane and the rotation was measured. All these data are shown in

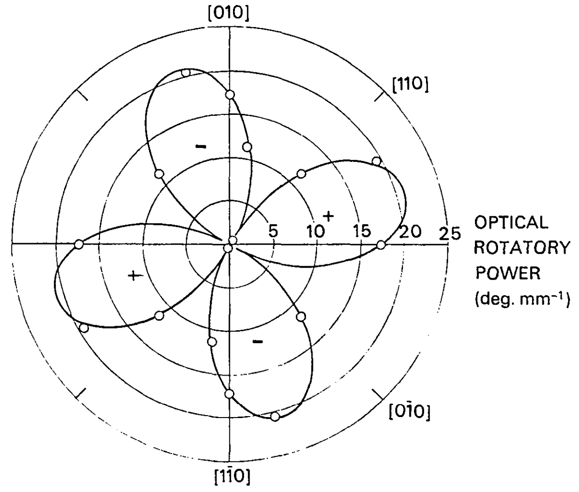

Fig. 4. The optical rotatory power for general directions in the (001) plane. The relationship between the sign of the rotation and the crystallographic labels are arbitrary to the extent that there is no convention for this crystal class as to which unit vector is [100].

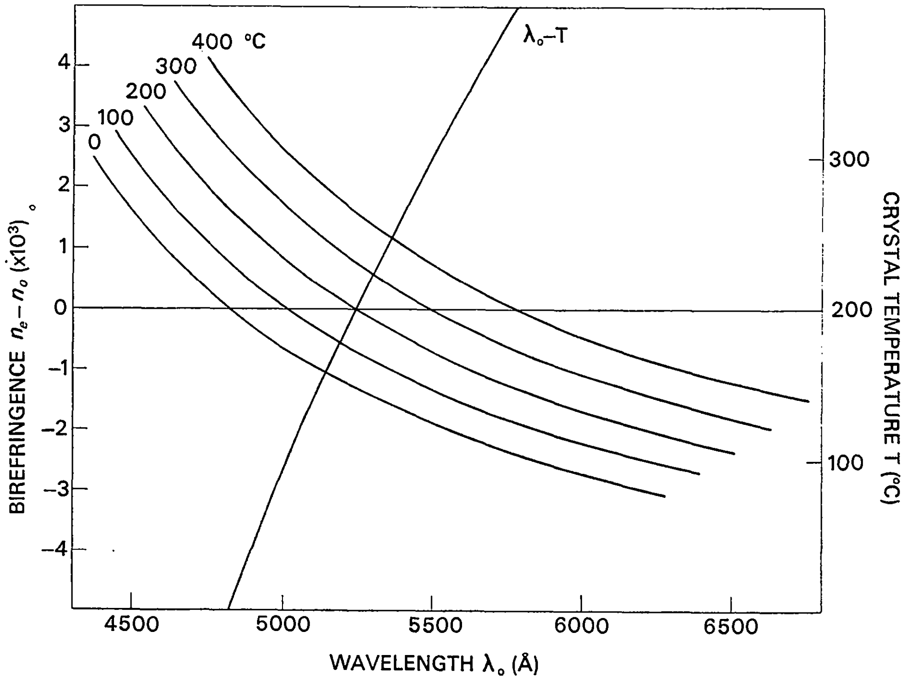

Fig. 5. The birefringence of $CdGa_2S_4$ for temperatures between 0 °C and 400 °C as a function of wavelength. The single curve gives the wavelength of the isotropy point as a function of the crystal temperature.

Fig. 4 together with the theoretical form based upon equation (2) and the *g* values derived above. Using plates cut normal to the *c* axis it was confirmed that there was no observable optical rotation for propagation along the $\bar{4}$ axis.

The temperature dependence of the optical properties of $CdGa_2S_4$

The weak birefringence of $CdGa_2S_4$ is sensitive to changes of temperature and it is possible to move the point of isotropy over a wide range of wavelengths. Measurements of the birefringence were made using the fringe technique up to 400 °C. From these measurements were derived the family of curves in Fig. 5 showing the birefringence at intervals of 100 °C as a function of wavelength. Also shown is the relationship of the wavelength for optical isotropy and the temperature. The point of isotropy varies from 4825 Å at 0 °C to 5780 Å at 400 °C; at room temperature $d\lambda/dT$ is about 1·85 Å deg^{-1}. It is probable that this function continues to hold to even higher temperatures thereby shifting the point of isotropy deep into the red part of the visible spectrum; cooling would probably not reduce the isotropy point much below 4500 Å. This 'thermal tuning' feature of the optical properties may prove of value in future studies or applications where a fixed isotropy point would be a severe limitation.

The optical rotatory power has been measured as a function of wavelength (and temperature) by shifting the isotropy point thermally. Fig. 6 shows that the magnitude of the effect in ⟨100⟩ directions decreased more rapidly than that in ⟨110⟩ directions. This implies that as the temperature and wavelength increase the four-lobed curve in Fig. 4 rotates in an anti-clockwise direction about the *c* axis and shrinks; this is permissible for crystals with $\bar{4}$ symmetry.

Optical activity and birefringence in $CdGa_2S_4$

It was shown by Hobden (1968*a*) that the existence of optical activity and birefringence in the vicinity of the isotropy point of $AgGaS_2$ gives bright fringes in the transmission spectrum when the crystal plates are placed in the 0° position between crossed polarizer and analyser. This phenomenom is also present in $CdGa_2S_4$ and is the most convenient method of demonstrating the effect of optical activity in these crystals. The light transmitted in these fringes is responsible for the light

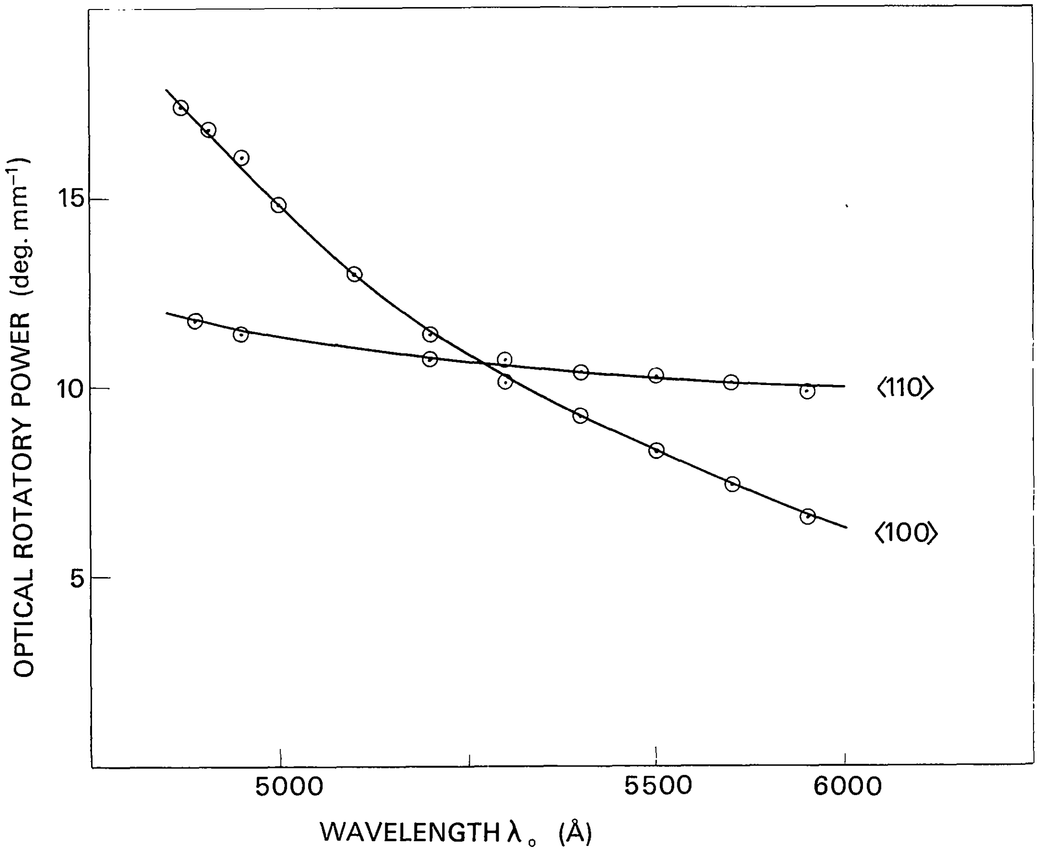

Fig. 6. The variation in the optical rotatory power at the point of isotropy as the point is isotropy of shifted to longerwavele ngths by raising the temperature.

blue incomplete extinction when the crystal plates are examined on the polarizing microscope in white light.

Conclusions

Optical activity has been observed for the first time in a crystal of class $\bar{4}$ and the effect has the correct directional properties for this symmetry. Optical activity has now been demonstrated in both of the enantiomorphous classes $\bar{4}$ and $\bar{4}2m$, and the original predictions of Gibbs (1882) have been confirmed (Hobden, 1968*a*).

The source of the effect and the reason for the difference in the magnitudes of the effect in $AgGaS_2$ (522 deg. mm^{-1}) and $CdGa_2S_4$ are still obscure. Calculations by Ramachandran's (1951*a*, *b*, *c*,) method based upon the interaction of point dipoles and using reasonable values of the atomic polarizabilities give optical rotatory powers for $AgGaS_2$ about two orders of magnitude too low. This shows that such a model is not suitable for these covalent tetrahedrally bonded compounds.

I would like to thank Mr D. S. Robertson for growing these crystals and Mr D. W. Brown for his assistance with this work .

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

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Elastic coefficients of an isotropic solid.

By T. S. G. Krishnamurty and V. Appalanarasimham, *Andhra University, Waltair, India*

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It is shown, on the basis of Jahn's method, that the conjecture made by one of us that there should be *n* *n*th order elastic coefficients of an isotropic solid does not hold good.

It is well known that elasticity expresses the relation between the applied stress and the resulting strain, both of which can be represented by the symmetric second rank tensors. Bhagavantam & Suryanarayana (1949) have employed the character method to derive the number of the non-vanishing independent elastic coefficients of orders 2 and 3 for the 32 classes of crystals. Identical results have been obtained by Jahn (1949) using the method of reduction of a representation. Recently Jahn's (1949) method has been extended by Krishnamurty & Gopalakrishnamurty (1968) to obtain the fourth- and fifth-order elastic coefficients in crystals. When the fourth-order elastic coefficients of crystals are enumerated by the character method, one of us (Krishnamurty, 1963) conjectured that the number of the *n*th order elastic coefficients, symmetric in all the *n* suffixes, of an isotropic solid (R_∞^i) would be *n*. In this note, it is shown that deviations from such a conjecture can arise from the elastic coefficients of orders higher than five.

If V denotes the representation of a polar vector and $[V^2]$ the symmetrical product (Tisza, 1933) of V with itself, then the *n*th order elastic coefficients, which are symmetric in all the n indices, are represented by $[[V^2]^n]$. In the reduced form of the representation, this contains terms of the type $[D_2^n]$, where D_2 is a five-dimensional representation. Some of the values of $[D_2^n]$, for $n>5$, may be easily derived and are given by

$$[D_2^6]=2D_0+2D_2+D_3+3D_4+D_5+3D_6+D_7+2D_8+D_9+D_{10}+D_{12}\,,$$

$$[D_2^7]=D_0+3D_2+D_3+3D_4+2D_5+3D_6+2D_7+3D_8+D_9+2D_{10}+D_{11}+D_{12}+D_{14}\,,$$

$$[D_2^8]=2D_0+3D_2+D_3+4D_4+2D_5+4D_6+2D_7+4D_8+2D_9+3D_{10}+D_{11}+2D_{12}+D_{13}+D_{14}+D_{16}\,,$$

$$[D_2^9]=2D_0+3D_2+2D_3+4D_4+2D_5+5D_6+3D_7+4D_8+3D_9+4D_{10}+2D_{11}+3D_{12}+D_{13}+2D_{14}+D_{15}+D_{16}+D_{18}\,,$$

and

$$[D_2^{10}]=2D_0+4D_2+D_3+5D_4+3D_5+5D_6+3D_7+6D_8+3D_9+5D_{10}+3D_{11}+4D_{12}+2D_{13}+3D_{14}+D_{15}+2D_{16}+D_{17}+D_{18}+D_{20}\,.$$

We observe that the coefficient of D_0 in each one of the above tabulated values is different from unity except in the case $n=7$. On the other hand, we know that the coefficient of D_0 in $[D_2^n]$ ($n=2$, 3, 4 and 5) is one (Jahn, 1949; Krishnamurty & Gopalakrishnamurty, 1968). It is these coefficients of D_0 in $[D_2^n]$ which are different from unity, that are responsible for the deviations in the conjecture referred to earlier.