Optically Anomalous Crystals

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TABLE OF CONTENTS

FOREWORD

WHAT ARE OPTICAL ANOMALIES?

Charles Darwin (Darwin, 1859), quoting one Professor Owen in the *Origin of Species*, said "There is no greater anomaly in nature than a bird that does not fly; yet there are several." If we were to construct a parallel, though more restricted statement about the objects of our interest, crystals, it would be something like this: "There is no greater anomaly in solid state science than a crystal without a unique symmetry; yet there are many." The present volume, *Optically Anomalous Crystals* by Alexander Shtukenberg and Yurii Punin, is devoted to the analysis of crystals with ill-defined symmetries whose pathologies are signaled by the unexpected effects that they impart to transmitted light. Such crystals have long puzzled scientists.

The problem posed by optically anomalous crystals was brilliantly summed up by Jaeger in his famous *Lectures on the Principle of Symmetry and Its Applications in All Natural Sciences* (Jaeger, 1917).

> With respect to their internal structure, crystals are objects whose behaviour is chiefly governed by the laws of symmetrical configuration. In general it may appear that no essential discordances exist between the external forms of each crystalline individual and its molecular structure; and the world of crystals appeared from this to be rigorously ruled by stubborn laws which do not allow any exception in the behavior of the individuals which have a part in it.
>
> However, on closer examination, this appears to be by no means the case under all circumstances. In this well-governed society too, with its clear lines of demarcation and its strictly defined distinctions of classes and systems, there are a number of individuals which behave certainly not as they should do. Numbers of eccentricities are to be noted, and the somewhat revolutionary manifestations of many individuals take place here in a similar degree, as in our much more insufficiently ruled human society.

It is nearly impossible to read Jaeger without the suspicion that he was reflecting on the events of Russia's contemporaneous, revolutionary year. This feeling becomes a certainty when examining the 1920 edition of *Lectures on the Principle of Symmetry*. The flush of the historic events faded, and with it, so did the revolutionary language. We cannot help but wonder what Jaeger would have made of the fact that our understanding of optically anomalous crystals would take its great leap forward with the publication of a book by scientists from the former Petrograd, only after languishing for the better part of a century. (Saint Petersburg State University, the one-time home of our authors, is just a stone throw across the Neva River from the Winter Palace, the home of the Romanovs.) Their inquiry derives importance from, and takes solace in, the longevity of optically anomalous crystals. As scientists, we can crow over the endurance of our enterprise, having quietly outlived the Soviet empire, and well on the way to outliving the American empire, however insufficiently ruled.

What is an *optically anomalous crystal*? Before answering this question we must distinguish between the term's literal interpretations and its typical usage. "Optically anomalous" has commonly been used to describe crystals that display *linear birefringence* under circumstances where we would not expect it. For example, if a cubic, optically isotropic crystal should become slightly deformed or desymmetrized by some mechanism—these will be discussed at length throughout—the crystal may become linearly birefringent and transmit light between crossed polarizers. Such a crystal would be quintessentially *optically anomalous*. If a centrosymmetric, triclinic crystal should lose its center of symmetry by the same mechanism, symmetry arguments tell us that such a crystal should be *circularly birefringent* and rotate the azimuth of applied, linearly polarized light. The second crystal would surely be optically anomalous in the literal sense. It would be optically rotatory despite the fact that the habit and x-ray structure may not show detectable deviations from centrosymmetry. However, the near impossibility of measuring small optical rotations reliably in triclinic systems (Kaminsky, 2000), obviates such examples. Given the overwhelming predominance of observations of anomalous linear birefringence as opposed to anomalous circular birefringence, or other effects such as linear or circular dichroism (although these phenomena are touched on herein), *optical anomaly*, has become synonymous with *anomalous linear birefringence* and we will use it as such unless otherwise specified.

BRIEF HISTORY OF OPTICAL ANOMALIES

The most striking features of crystals are their symmetric, polyhedral forms. Federov said that crystals "flash-forth their symmetry" (Shubnikov and Kopstik, 1974), a strong allusion to the sharp, highly reflecting surfaces of well-formed crystals prized by enthusiasts. We learned from Häuy that the shapes of crystals reflect the arrangements of the particles from which they are constructed. Today, these arrangements are routinely deduced from x-ray diffraction patterns. In the 19th Century, prior to the discovery of x-rays, the perturbations to the state of visible light traversing a crystal were used to assay symmetry.

Ideally, the symmetry of a crystal that an investigator would deduce from shape, from the transmission of visible light, from the scattering of x-rays, or from any other method, should be the same. However, as early as 1818, David Brewster in Edinburgh first noticed that some crystals appeared to have lower optical symmetries than morphological symmetries (Brewster, 1818b).

> Philosophers will no doubt be surprised to learn, that *muriate of soda, fluate of lime, the Diamond, Alum* have actually the property of Double Refraction, but under circumstances of such a singular kind, as to entitle them to be regarded as a new class of doubly refracting crystals.

Shown in Figure 1 are typical examples of anomalous birefringence in diamond cut perpendicular to the three-fold axis (Figure 1a) and the four-fold axis (Figure 1b). The false color scale is related to the birefringence in these images (Glazer *et al.*, 1996). While the birefringence is heterogeneous is both cases, in (*a*) it forms a well-defined pattern while in (*b*) the property is scattered throughout in a helter-skelter arrangement. The images in Figure 1 were made with a contemporary birefringence imaging device. However, Brewster recorded comparable patterns hand-drawn from his observations through a microscope crudely fitted with polarizers (Brewster, 1835).

In his attempt to understand these strange specimens of otherwise cubic crystals, Brewster enlisted the assistance of the greatest contemporary mineralogist/chemist, Jöns Jakob Berzelius, who concluded, after extensive chemical analyses, that optically anomalous and optically normal crystals of the same ostensible species were composed of the same constituents. On this basis, Berzelius minimized the importance of the optical differences. Brewster's retort, in its essence, contained the argument that the elemental analyses of an ostrich and an eagle might be indistinguishable, but that doesn't mean both will fly (Brewster, 1822).

Theories offered to explain away inconsistencies in optical and morphological symmetry emerged in France. Biot (1842) and then Mallard (1886) speculated that symmetrical forms might arise from dissymmetric individuals via the twinning of lamellae. In Germany, Klocke and Klein favored explanations that resulted from strain induced in high-symmetry minerals through tectonic forces or during rapid crystallization. Arguments in the literature were spirited, and became mean-spirited during and after the Franco-Prussian war (Kahr and McBride, 1992).

The debate concerning the etiology of anomalous birefringence had become so confused that a scientific society in Leipzig sponsored a prize competition aimed at settling this contentious issue. The prize was awarded to Marburg privatdozent Reinhard Brauns, whose comprehensive 380 page book *Die optischen Anomalien der Krystalle* was published in 1891 (Brauns, 1891). Brauns presented discussions of some six dozen anomalously birefringent substances (Figure 2). The book presented research on optically anomalous crystals as a closed subject by parsing the list of optically anomalous substances among categories that represented the various proposed etiologies.

Gustav Tammann (1917), speculated that although internal stress from impurities should play a role, the ordering of components alone would suffice to cause birefringence. He indicated that such arrangements resulted from kinetic, not thermodynamic, control of crystal growth, whereby sites that would otherwise be related by symmetry have not had time to reach equilibrium.

When the discovery of x-ray diffraction transformed crystallography in 1912, several investigators tried to find a substantial difference in the atomic structures of optically anomalous and optical normal crystals of the same species. Given the qualitative methods of intensity analysis available in the two decades following the Braggs' first x-ray crystal structures, these searches were doomed to fail. In this

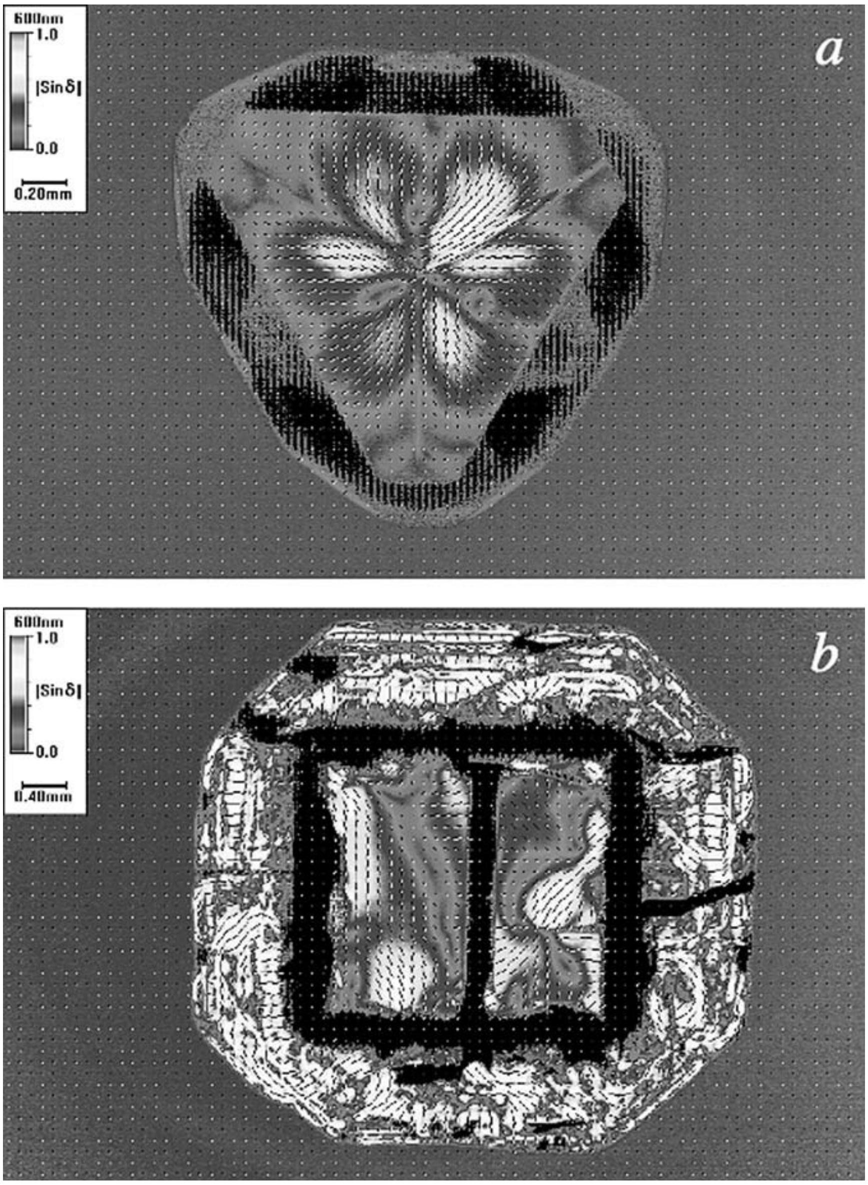

Figure 1. Anomalous birefringence images of sections of diamond cut (*a*) perpendicular to the threefold axis, and (*b*) perpendicular to the fourfold axis. The false color scale plotted as $|\sin\delta|$ where $\delta = 2\pi\Delta nL/\lambda$, $\Delta n = n_{\perp} - n_{\parallel}$, L is the sample thickness, and λ is the wavelength of light. Hash marks indicate the extinction directions, the orientation of the most refracting directions
Source: Figure courtesy of Dr. M. Geday (see Color Section following page 254)

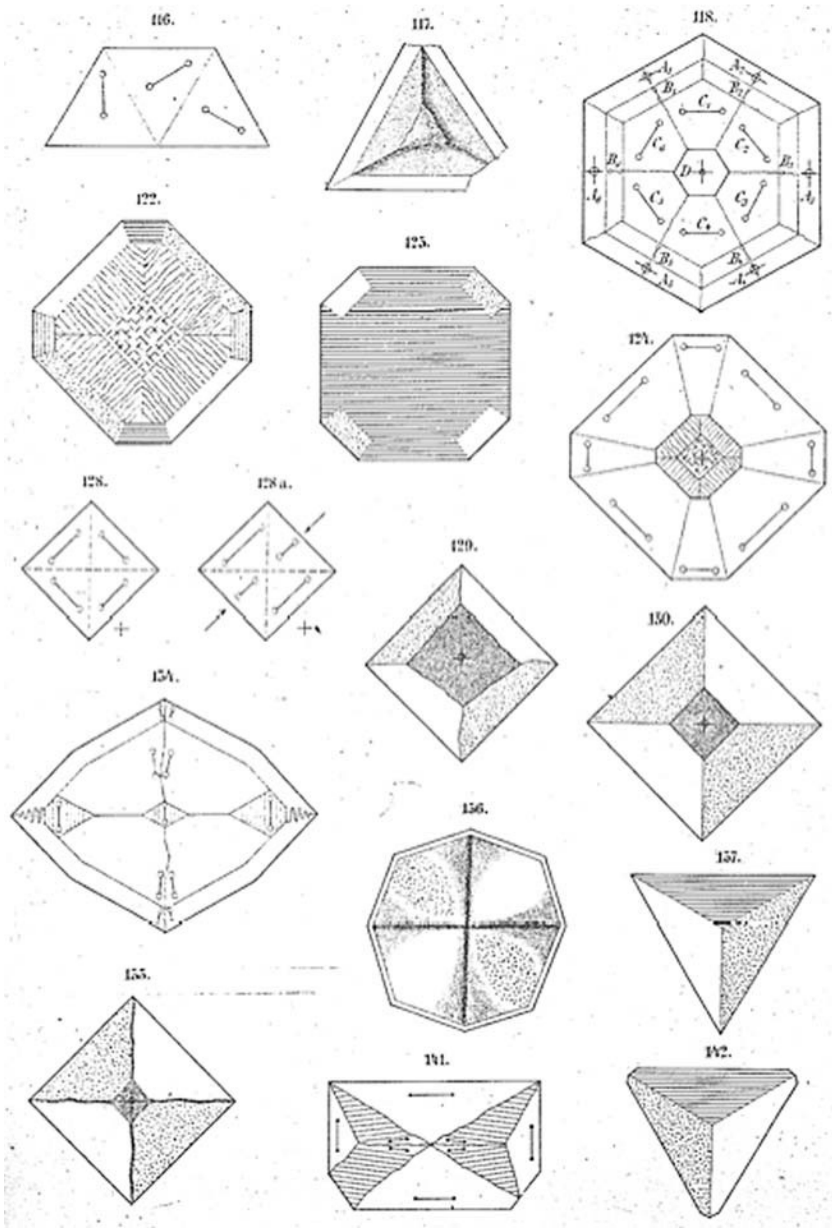

Figure 2. Typical array of optically anomalous crystals from Brauns' *Die optischen Anomalien der Krystalle* (1891)
Source: From Brauns, R. *Die Optischen Anomalien der Krystalle*; S. Hirzel: Leipzig, 1891.

new climate, the insights of Tammann fell largely on deaf ears. The community of crystallographers was focused on fixing the positions of atoms.

NEUMANN-CURIE PRINCIPLE

Optically anomalous crystals appear to violate Pierre Curie's Symmetry Principle, one of the most general and powerful organizing concepts in the physical sciences. The Curie Symmetry Principle, when applied to problems in crystal physics, is usually referred to as the Neumann-Curie Principle after one of its progenitors, Franz Neumann. It states that the properties of a system are invariant to its symmetry operations. Curie asserted the impossibility of bringing about certain effects under circumstances lacking essential dissymmetries that are characteristic of the effects.

A contemporary articulation of the Symmetry Principle would embody the following statements:

1. The symmetry elements of a cause must reappear in the effects it produces.
2. Dissymmetric effects must be evident in the cause from which they arise.
3. The converse of the previous statements must hold: Effects can be more symmetrical than their associated causes.

The Neumann-Curie Principle has its origins in the classification of crystals according to their effects on transmitted light. Réné Just Haüy recognized in 1792 that only crystals with the forms of the cube, octahedron, or rhombic dodecahedron were isotropic with respect to light refraction (Burke, 1966). Haüy did not make distinctions within the class of optically anisotropic crystals. This was accomplished simultaneously by Brewster (1818a) and Biot (1818), following the discovery of light polarization by reflection. They were now equipped to exploit the observation of interference in some crystals as sensitive signatures of anisotropy, and thus began the real work of classifying crystals optically. Brewster and Biot succeeded in partitioning anisotropic crystals into the uniaxial (trigonal, tetragonal, and hexagonal) and biaxial (less than threefold symmetry) classes, indicating the numbers of directions characterized by polarization independent refraction. The wavelength dependence of the refractive index, dispersion, ultimately enabled a distinction among biaxial crystals with zero, one, or three directions fixed by symmetry for all wavelengths. This brought the total number of optical classes to five.

An account of the conceptual development of the Neumann–Curie Principle is continued by Shubnikov and Kopstik (1974). To Vivell (1830) they attribute the following statement: "the optical symmetry of crystals corresponds to their geometric symmetry." Neumann generalized the principle of Vivell by claiming that "in all its physical properties, a material exhibits the same kind of symmetry as its crystallographic shape" (Neumann, 1841). This message was carried forward by his pupil Minnigerode, who abandoned shape as a point of reference: "the symmetry group of a crystal is a subgroup of the symmetry groups of all the physical phenomena which may possibly occur in that crystal." Pierre Curie went one step further by replacing "crystal" with "medium" (Curie, 1894). Ultimately, Woldemar Voigt, another Neumann student, systematized the Symmetry Principle in crystal physics by introducing tensor notation (Voigt, 1910).

What is remarkable to this observer in hindsight is that just as Brewster and Biot were developing their optical classification of crystals on the basis of symmetry, they were focusing also on the exceptions, the so-called optically anomalous crystals. Despite the fact that there were many crystals that seemed to have inconsistent optical and morphological symmetries, faith in the developing Symmetry Principle—whether fully articulated or just intuitive—gave researchers the confidence to push on with the symmetry-based classification of crystals certain that explanations for the anomalies would arrive in due course. This has not necessarily been the case.

DIE OPTISCHEN ANOMALIEN DER KRISTALLE

The high water mark in the study of optical anomalies, prior to the publication of the present volume, was Brauns' book from 1891 (Brauns, 1891). Here, we have the opportunity to make a unique comparison between *Die optischen Anomalien der Kristalle* by Brauns, and *Optically Anomalous Crystals* by Shtukenberg and Punin, the only two monographs on a subject between which sits the entire 20th Century.

Brauns created six classes of optical anomalies.

1. Optical anomalies due to differently crossed lamellae.
2. Optical anomalies due to dimorphism (the coexistence of more than one phase).
3. Optical anomalies due to mechanical pressure, rapid cooling, etc. (by the etc. Brauns was invoking any harsh treatment during the life of the crystal).
4. Optical anomalies due to isomorphous admixtures (and the strain induced by the mismatch of components).
5. Optical anomalies as a result of efflorescence.
6. Optical anomalies whose cause is not known or which do not fit into any of the above categories.

Brauns encapsulated all the experimental and theoretical observations on optical anomalies within a single volume and in doing so he may have given his work more authority than it merited. Subsequent writers frequently cited *Die optischen Anomalien* as the definitive source on the subject. Many of Brauns' assignments therefore went unchallenged.

How does Brauns's presentation and classification square with the revelations of the present reanalysis? After a brief introduction to classical crystal optics and the interaction of light and matter, in Chapter 1, Shtukenberg and Punin discuss in depth photoelastic and/or piezo-optic sources of optical anomalies in Chapter 2. This overlaps with observations in Brauns' classes #2 and #3. In Chapter 3, the kinetic ordering of constituents during growth is modeled, leading to impressive predictions of the optical distortions to be expected as a function of growth rates and temperatures; optical properties are connected to activation parameters. Kinetic order often requires admixture and here the overlap is largely with class #4. Anomalies due to heterogeneities in lamellar crystals and other complex accretions is taken up in Chapter 4. Comparisons can be made to materials in class #1. While there is surely no one-to-one correspondence of themes, we see the vindication of the main ideas of Brauns and his progenitors in one way or another, in one substance or another. Like the final category of *Die optischen Anomalien*, Chapter 5 tackles the vexing confluence and interplay of the variety of sources of optical anomalies.

Optically Anomalous Crystals departs from the format of Brauns, in that it does not attempt to digest all that is known for each known optically anomalous crystal. Given the exponential growth of the scientific literature over the past century and the discovery of many new optically anomalous substances, Brauns's 380-page treatise could easily fill 3,800 comparable, contemporary pages. Rather, the strength of Shtukenberg and Punin's book is the development of quantitative models based on in-depth analyses of a smaller number of substances. One family of minerals, the garnets, and one family of water-soluble salts, the alums, are treated exhaustively, and many other systems are treated in lesser detail. The presentation is largely based on research that comes from the authors' laboratories. However, the generality of the models developed enable their application to almost any substance.

What naturally distinguishes Shtukenberg and Punin from Brauns is an extra century experience and sophistication. The concepts that the present authors can draw upon that were unknown in 1891 include the following: the tensorial description of physical properties, the enumerations of the space groups, x-ray diffraction, the spiral crystal growth mechanism, transition state theory, the theory and direct observations of dislocations.

The mission of Shtukenberg and Punin can be likened to that of physicians. The crystal sections in Figure 1 both show optical anomalies but their strikingly different character is evidence of distinct origins. It is the job of the optical crystallographer to properly characterize the symptoms (the anomalous birefringence), propose a disease (strain, kinetic ordering, etc.), and then find evidence for it (dislocations, selective atoms occupancies, etc.). Sometimes, it is obvious that a patient is gravely ill, but the origin of the malady can be extraordinary subtle. Perhaps, one amino acid of one enzyme is not what it should be. As with optically anomalous crystals, it is often obvious that something is "wrong", but the challenge, which can captivate, is diagnosing the illness. The full sweep of developments in solid state science in the twentieth century were requisite for the accounting of optically anomalous crystals contained herein. Brauns, like a nineteenth century physician, similarly without x-rays, was by and large shooting in the dark.

Optically Anomalous Crystals was first published in Russian by Nauka in 2004 (Shtukenberg and Punin, 2004). Conspicuously absent from that work are molecular/organic crystals, not a part of the mineralogy. Likewise, Brauns barely touches molecular crystals.He discussed only one organic crystal, strychnine sulfate hexahydrate. Moreover, he isolates strychnine—perhaps he was afraid of it—in a class by itself. Strychnine sulfate ($C_{21}H_{24}O_6N_2S \cdot 6H_2O$) hexahydrate was optical anomalies class #5, the singular substance that became anomalous due to the loss of solvent. However, as *Die optischen Anomalien* went to press, Martin (1891) completed a thesis on optically anomalous organics. Many others have been found, and we have added, a discussion of several organic examples to the present volume where most appropriate.

Large, polyfunctional organic molecules may at first blush seem to complicate many of the ideas and models put forward throughout. However, the size of organic molecules amplifies surface topography and simplifies arguments based upon shape. Moreover, intuitive judgments about intermolecular interactions are supported in polyfunctional organic molecules that are much more difficult to formulate with monatomic, or simple, symmetrical polyatomic ions.

OPTICAL ANOMALIES EXCLUDED

As with any finite investigation in the natural sciences, authors must establish boundaries and the more fully explained are the choices of boundaries, the less arbitrary they may seem. The following discussion is restricted to the 32 classical crystal point groups of the Nineteenth Century, those involving rotational symmetries of 2π, π, $2\pi/3$, $\pi/2$, and $\pi/3$. The International Union of Crystallography has subsequently broadened the definition of a crystal so as to include aperiodic materials (Report of the Ad Interim Commission on Aperiodic Crystals, 1992) with impossible rotational symmetries of order 5, 7, 8, 10, 12…the beautiful subject quasicrystals (Steuer, 2004). Presently, there is little information on the refractivity of quasicrystals save for a prediction of a negative index of refraction in 12-fold symmetric quasicrystals (Feng *et al.*, 2005). Despite the fact that negative indices of refraction, previously considered to be an impossibility but now rather firmly established, are perhaps the ultimate optical anomalies, negative refraction in 12-fold symmetric quasicrystals takes us immeasurably far afield of the subject of our interest, unexpected linear birefringence of visible light in crystals of common experience.

Likewise, omitted from this book is a discussion of the magnetic crystal point groups, or more generally the Shubnikov two color groups. These groups are necessary in order to fully describe the birefringence of magnetic boracites containing Co and Ni (Mao *et al.*, 1999) Boracite, most commonly $Mg_7Cl_2B_{16}O_{30}$, is ostensibly cubic but its birefringence was reported in 1821 by Brewster (Anonymous, 1821) just a few years after launching the study of anomalous birefringence. Given the dizzying interplay of ferromagnetism, ferroelectricity, and ferroelasticity in these crystals, each of which is manifested directly and/or indirectly on the optical indicatrix of individual domains, the optics are expected to be extraordinarily complex, however they do not necessarily fall under the banner of *anomalous*.

Jones (1948) recognized certain symmetries in the formal expression of crystal optics that argue for a second pair of extinction or absorption axes bisecting the usual ones. Graham and Raab (1983) predicted circumstances and magnitudes of so-called “Jones birefringence” and “Jones dichroism”. Lorentz predicted that some cubic crystals could be weakly birefringent because of the non-uniformity of the electric field of a plane wave across a unit cell

(Lorentz, 1936; Agranovich and Ginzburg, 1984). We can say that Jones birefringence and the Lorentz effect are surely *unusual* examples of birefringence, but they would not qualify as optical anomalies.

The inquiry of Shtukenberg and Punin is restricted to linear optical anomalies. Even though precisely the same processes of desymmetrization that may give rise to linear birefringence in an otherwise isotropic crystal may give rise to second harmonic generation in an otherwise centrosymmetric crystal (Weissbuch *et al*., 1989), *Optically Anomalous Crystals* is restricted to phenomena made manifest in modest electric fields from incandescent light sources, as the subject is rooted in classical, linear crystal optics.

Google will find innumerable uses of *optical anomaly* in the scientific literature. For example, Overhauser and Butler (1976) wrote about the optical anomaly in the reflection spectrum of potassium metal that is induced by a surface layer of KOH causing a distortion of the optical indicatrix of the metal. Why is this not a fitting subject of *Optically Anomalous Crystals*? It might be. Its grounds for disqualification are soft at best. The study of optical anomalies is closely related to mineralogy and the use of the polarized light microscope to study birefringence in transmission. Potassium metal does not occur naturally, it is studied in reflection, indicatrix distortion is detected by absorption, and the problem is disconnected from the rich tradition of optical anomalies.

OPTICALLY ANOMALOUS CRYSTALS *FROM RUSSIA*

The study of optically anomalous crystals began in Scotland, moved to France, reached its zenith in Germany, and then expired. The themes of optical anomalies, particular those due to kinetic ordering, reemerged among scientists from Israel, Japan, and the United States among other places, in the 1980's and 1990's. Unfortunately, this mini-renaissance passed over a number of seminal contributions, elaborated herein, first published in Russian in the 1960s and 1970s. A history of optically anomalous crystals that attempted to be comprehensive (Kahr and McBride, 1992) missed some essential Russian papers. This is an unfortunate consequence of the increasingly Anglo-centric scientific enterprise that time and again overlooks more than half of the world that does not use the Roman alphabet.

Shubnikov, a serious student of Pierre Curie (Shubnikov, 1988) first articulated the idea that growth pyramids, those sub-volumes of a crystal whose bases represent the growing faces and whose coincident apices mark the site of nucleation, must have a reduced symmetry (Shubnikov, 1961). Such faces cannot have cubic symmetry; that would require symmetry axes not normal to the faces. They can not be centrosymmetric; inside is the crystal, while outside is the growth medium. In fact, such faces can only admit ten point groups: 1, 2, 3, 4, 6, m, $2mm$, $3m$, $4mm$, $6mm$. Shubnikov recognized that crystals with geometrically polar growth sectors could, in principle, display polar properties even when the idealized structure of the medium was centric. He further realized that cubic crystals with dissymmetric pyramids could lead to double refraction or double absorption, or any number of other properties. He did not discuss in detail the mechanisms of desymmetrization, but he did, on the basis of symmetry, presuppose the process of kinetic growth desymmetrization discussed in detail in Chapter 3. A rigorous group theoretical analysis of the symmetry reduction inherent in mixed crystal growth is also provided in Chapter 3.

Immediately thereafter, Tsinober and coworkers began a series of investigations into the anomalous pleochroism of smoky quartz and amethyst (Tsinober, 1962). On the basis of single crystal ESR intensity measurements it was established that these crystals trap Al^{3+} and Fe^{3+} in three crystallographically equivalent silicon positions that are not translationally related on the growth face. When adsorbed to the $\{01\bar{1}1\}$ and $\{\bar{1}\bar{1}20\}$ sectors of surface symmetry 1 and 2, respectively, the corresponding pyramids were biaxial with anomalous pleochroism, whereas the {0001} sectors of symmetry 3 were uniaxial showing ordinary dichroism (Tsinober *et al*., 1967a). A slightly different explanation was offered more recently (Partlow and Cohen, 1986). The local symmetry of growth active faces was used to interpret optically anomalous cordierite $Al_3Mg_2(Si_5AlO_{18})$ (Tsinober *et al*., 1977). Similar analyses were applied to quartz, (Tsinober and Samoilovich, 1975), zinc selenate (Nizamutdinov *et al*., 1977) and sodium kröhnkite $Na_2Cu(SO_4)_2 \cdot 2H_2O$ (Vinokurov *et al*., 1977).

THE ABOLITION OF OPTICAL ANOMALIES?

As we will see in Chapter 1, properties of crystals can be evaluated classically or even quantum mechanically, using first principles applied to crystal structures. Given this rather complete understanding of crystal physics, optical anomalies should not exist. However, crystals often display distortions of structure that cannot be revealed by standard methods of analysis or are often overlooked/ignored by researchers. Because subtle structural distortions can profoundly influence optical manifestations of crystals, the study of optically anomalous crystals has endured for almost two centuries.

Are optical anomalies in the eyes of the beholder? One investigator's anomaly may be an expectation for another more knowledgeable or more sophisticated scientist. An über-investigator with the wherewithal to characterize a crystalline substance by any means necessary to the greatest conceivable effect would witness the melting away of anomalies. They would be replaced by a more nuanced understanding of the structure and physical properties. Anomalies are supported by a measure of ignorance. This is why the study of optically anomalous crystals flourished at the end of the nineteenth century prior to the discovery of x-ray diffraction, when the analysis of crystal structure and properties was circumscribed by light microscopy. In the absence of complementary methods of structure determination, investigators were free to inject their well-earned prejudices into the debate. To the extent that Shtukenberg and Punin have succeeded in their purpose, this book, or at least large parts of it, could be called *Formerly Optically Anomalous Crystals*. For example, we now know from x-ray analysis that chlorate and bromate ions in mixed sodium salts are not statistically distributed among lattice sites otherwise related by symmetry in the cubic space group $P2_13$. Thus, the observation of birefringent cubes is no longer vexing (Gopalan *et al.*, 1993; Shtukenberg *et al.*, 2004). However, birefringence in mixed sodium halates has long been considered anomalous. It is discussed at length by Brauns (1891), and classified in the "not sure" class #6. As such, the mixed halates are likewise considered herein.

On the other hand, investigators run the danger of seeing etiologies of anomalous birefringence in data from methods of analysis that complement the light microscope when the evidence may not really be substantial. Akizuki, a pioneer in the study of optically anomalous silicates, and his coworkers (Tanaka *et al.*, 2002b) observed a monoclinic optical indicatrix in the {011} growth sectors of yugawaralite ($CaAl_2Si_6O_{16} \cdot 4H_2O$). The {120} sectors were optically triclinic. x-ray data from single growth sectors supported this difference. However, when the data was re-analyzed by Baur and Fischer (2002), lattice constants and interatomic distances were not found to be significantly different, while systematic absences were maintained in the triclinic dataset. The optical analysis tells us that the sectors are monoclinic and triclinic but that doesn't mean that the nature of the deviations from symmetry can be precisely defined. The light microscope, old as it may be, is astonishingly sensitive to small deviations in symmetry. It is for this reason that optically anomalous crystals will continue to test the ingenuity of crystallographers for another century at least.

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