tained from the four diamagnetic orthosilicates listed in Table 1.

A similar procedure can be used to estimate the entropy of the garnet almandine. Using grossularite as the reference compound in Eq. 2, we obtain an estimated lattice entropy for almandine of 60.34 gibbs/mole. Since $S = 2$ for Fe^{2+}, the magnetic entropy (from Eq. 3) is 9.59 gibbs per mole (that is, 3 g-atoms). Thus, the estimated entropy at 298.15°K is $60.34 + 9.59 = 69.93$ gibbs/mole, a value somewhat greater than the 68.13 gibbs/mole estimated by Saxena (*1*).

It is instructive to compare Saxena's correlation with the methods given here for estimating the entropy of another garnet. For andradite ($Ca_3Fe_2Si_3O_{12}$), the entropy at 298.15°K (78.7 ± 1.3 gibbs/mole) has been computed (*6*) from heat capacity data (*7*). The molar volume, 131.65 cm³, is obtained from the unit cell parameter, 12.048 Å, given in Wyckoff (*8*). The substitution of 131.65 cm³ in equation 2 of Saxena (*1*) yields an entropy of 94.32 gibbs/mole. Since $S = 5/2$ for Fe^{3+}, $S_m = 2R \ln 6 = 7.12$ gibbs/mole. If grossularite is used as the reference compound in Eq. 2, we obtain 66.85 gibbs/mole as the lattice entropy of andradite; this added to the magnetic entropy gives an entropy of 73.97 gibbs/mole, an estimate much closer to the experimental value than is predicted from (*1*). This example amply illustrates the pitfall of estimating entropy from volume alone.

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My report (*1*) was written primarily in an effort to develop an empirical relationship between the molar volume and entropy $\bar{S}$ of silicates that would yield somewhat better estimates of third law entropies than those obtained by the summation of the entropies of the constituent oxides. It still serves that purpose for silicates of nontransition elements. The entropy-volume relation (*1*) was found to be particularly good for silicates with spherical ions, a point that I emphasized. I did not consider the transition elements because of a lack of data, although I did discuss the entropy of almandine on the basis of the data on Fe_2SiO_4 and Mn_2SiO_4.

Table 1. Comparison of the entropy estimates of silicates by three different methods. Averages of the constant A used [equation 1 of (*2*)] are −134.47, −87.67, and −283.33 gibbs/mole for ortho-, meta-, and framework silicates, respectively. Abbreviations: exp, experimental; calc, calculated; oxides, oxide summation; N.P., not possible without more data.

Silicate	$S_{exp} - S_{calc}$		$S_{exp} - S_{oxides}$
	Saxena	Cantor	
	Orthosilicates		
Be_2SiO_4	0.14	1.46	−1.25
β-Ca_2SiO_4	0.33	2.75	1.62
γ-Ca_2SiO_4	−9.15	−0.84	−0.08
Mg_2SiO_4	0.67	1.50	−0.01
Zn_2SiO_4	0.38	−1.94	0.66
$Ca_3Al_2Si_3O_{12}$	−2.25	N.P.	−12.63
½($Ca_3MgSi_2O_8$)	−1.53	+3.24	−4.54
	Metasilicates		
$CaSiO_3$	−0.97	−0.83	0.22
$CaSiO_3$ (pseudo)	0.25	0.44	1.08
$CaAlAlSiO_6$	2.36	0.18	3.04
$CaMgSi_2O_6$	0.54	−0.80	−1.50
$MgSiO_3$	0.25	0.33	−0.10
$NaAlSi_2O_6$	1.35	0.72	−2.94
	Feldspars and feldspathoids		
$KAlSi_3O_8$ (microcline)	0.03	−3.27	5.49
$KAlSi_3O_8$ (sanidine)	0.11	−3.37	5.52
$NaAlSi_3O_8$ (low albite)	1.30	−1.11	5.48
$NaAlSi_3O_8$ (high albite)	1.15	−1.20	5.48

It is well known that for spherical ions there is a distinct correlation between mass and volume. The significant correlation found between the entropy and volume of the silicates indirectly attests to this fact. It was my hope that Cantor's (*2*) equations would provide significant improvement in the entropy estimates. Unfortunately, Table 1 shows that this is not true. Cantor's (*2*) calculated entropies of almandine and pyrope (69.93 and 47.07 gibbs/mole, respectively) also do not differ significantly from mine (68.13 and 47.47, respectively). As I discussed in (*1*), equation 2 was based on only two entropy values and therefore should not generally be used without additional data. Table 2 shows that for silicates of transition metals the entropy estimates of Cantor (*2*) are no better than those obtained by the oxide summation method.

Table 2. Comparison of the entropy estimates of silicates of transition metal ions.

Silicate	$S_{exp} - S_{calc}$ (Cantor)	$S_{exp} - S_{oxides}$
Fe_2SiO_4	−0.78	−1.95
Mn_2SiO_4	1.58	0.58
$Ca_3Fe_2Si_3O_{12}$	4.73	−0.06

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20 June 1977

Checkerboards and Color Aftereffects

The cover of the 9 April 1976 issue of *Science* (*1*) purports to show that the human visual system analyzes patterns into Fourier components rather than into local features. As such, the demonstration is quite misleading since it can be understood on rather more simple grounds. There has, indeed, been rather substantial experimental evidence to suggest that the eye may behave in this way, although the matter is still controversial. At issue is not whether a Fourier representation of visual space can be useful in studying visual phenomena (the answer is a clear yes), but whether signals moving in the optic nerve from retina to cortex are coded in terms of a Fourier analysis of a scene rather than in some more straightforward representation.

To ask for the Fourier components of a scene is to ask to what degree the scene can be regarded as a linear superposition of periodic patterns of long bars (the component bars, strictly speaking, being sinusoidal rather than square-wave in form). It is a multidimensional problem since we must consider all possible orientations of the bars. We do not need mathematics, however, to see that a checkerboard has no periodic components of this kind parallel to its edges, but that it does have a clearly periodic character along the diagonals.

Consider a checkerboard pattern with grid edges arranged vertically and horizontally. We might at first expect to find in the patterns vertical and horizontal periodicity of the kind described above. That we do not can be qualitatively understood by imagining the pattern to be scanned with a set of long, but very narrow, uniformly but variably spaced slits parallel to one set of edges. It is clear that regardless of the slit spacing there can be no change in total light flux through the slits as the black and white squares contribute canceling elements along each slit. However, if the same "comb" is scanned across the checkerboard at 45° a strong periodicity can be found. It is immediately clear without recourse to mathematics that the function is a triangular with a period of $\sqrt{2}$ times the checkerboard square dimension. This is consistent with the results of Kelly (2) who has shown that there are, in addition, weak periodic elements at orientations between 0° and 45°. (Our comb model will easily find the orientations and periods of these components in order of decreasing strength, and, though with more difficulty, their numerical relative strengths.)

The visual meaning of this can be made clear by holding the cover illustration horizontally at comfortable arm's length a little below eye level. If the figure is now rotated about a vertical axis, a shallowly oblique view reveals the appearance of a strong bar pattern when looking along the diagonals of the squares, but virtually no periodicity when looking along the principal directions. In the latter case, the eye may, however, see a trace of apparent periodicity because, unlike our imagined slits, it does not integrate completely along the length of the bar. The periodicity along the diagonal can also be clearly seen by viewing the pattern in an out-of-focus fashion.

On the *Science* cover, the checkerboard is positioned at 45°, so that these periodic components appear in the vertical (and horizontal) direction. The spacing of these vertical bands is almost identical to the spacing of the bars in the (upper right) narrower pattern. It is therefore hardly mysterious that they appear to match this pattern more closely than they appear to match the coarser grating at upper left.

The Fourier approach, used intuitively or formally, is adequate and useful to describe the scene. It simply tells us where the dark and light is (if we do not take the trouble to look), and that, in gross appearance, a checkerboard should appear visually as if it consisted of grids of dark and light bars along the diagonals of its elements. Indeed the results of May and Matteson (3) and of Green *et al.* (1) are quite consistent with such a simple picture. These experiments and the cover illustration neither confirm nor deny the possibility of Fourier "channels" in the visual system.

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Green *et al.* (1) and May and Matteson (2) have implicated Fourier analysis in the McCollough (3) effects obtained from checkerboard patterns. In a clever experimental design they found that the color contingent aftereffect seen in a simple grating was oriented not with the edges in the checkerboard pattern but with the fundamental Fourier component, which is oriented at 45° from the actual edges. Both groups of investigators imply that their experiments make the distinction between an edge detector and a Fourier model of the pattern perception underlying color contingent aftereffects, but they have not considered the functions of known types of receptive fields in response to the checkerboard stimulus.

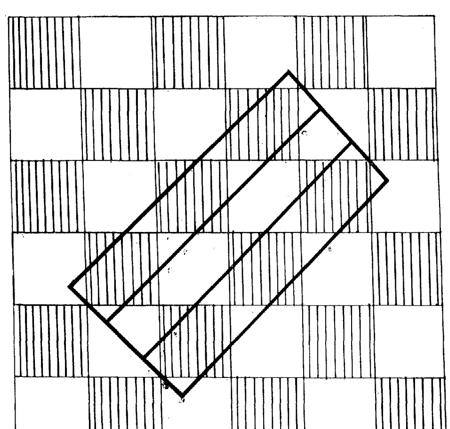

Fig. 1. Depiction of a typical receptive field onto which the checkerboard stimulus is projected. Note that the mean luminance in the central region is much higher than the two flanking regions, providing good stimulation of this oblique receptive field by the checkerboard.

I first want to establish that a typical elongated cortical receptive field can exhibit the behavior described in the checkerboard McCollough effect. If an elongated field happens to be three or four times larger than the squares in the checkerboard, then an alignment parallel with the edges of the squares will cover several squares, with a resultant stimulation approximately equal to the mean luminance of the checkerboard stimulus. But if it is aligned along a diagonal, the elongated center of the receptive field can be stimulated to a much greater or much less extent than the mean luminance, depending on whether it falls on a dark or a light diagonal, and the surround regions of the receptive field can fall on the opposing contrast diagonal, further enhancing this effect. Thus, a classic type of receptive field can readily produce the paradoxical oblique McCollough effect (assuming it is appropriately color-coded). Furthermore, the geometry of the situation is such as to produce a size (spatial frequency) shift, as described by one group, since the average width across light or dark diagonals is $\sqrt{2}$ less than the width of the squares (see Fig. 1).

One reason to expect the diagonals to predominate in effects involving chromatic channels is the poor spatial resolution of chromatic channels (4) measured by the detection of chromatic gratings. The simplest physiological explanation for this poor resolution is that predominantly large receptive fields exist for the detection of spatial chromatic organization (that is, colored edges). Thus, elements of the checkerboard pattern that best stimulate large receptive fields will have the greatest effect in the McCollough-type induction. The largest elements are those described by the lowest spatial frequencies, that is, the diagonal lines of checks. Hence previous evidence concerning the organization of the chromatic system would lead to the prediction of predominance of the diagonals in the checkerboard McCollough effect, without invoking the concept of a neural Fourier analysis. Of course, large receptive fields could also occur in the achromatic channels, producing oblique effects for achromatic adaptation.

Green *et al.* comment that it is the

diagonals which are actually most visible in the display, in contrast to my report (*5*) that perception of the diagonals tends to be perceptually suppressed. This is probably not a contradiction, as the suppression is only observed under the following controlled conditions: (1) the pattern projects to a homogeneous retinal area, (ii) the contrast magnitudes of the Fourier components are set to control for the contrast sensitivity limitations of the human visual system, and (iii) the oblique effect is controlled. Observation of their checkerboard stimulus shows that the diagonals are suppressed around the point of fixation, but not in peripheral regard where poor optical and retinal resolution will tend to degrade the sharpness of the edges. However, if this low spatial frequency suppression is present in the McCollough checkerboard effect, it might tend to reduce the predominance of oblique orientations. One reason that this suppression may not occur in color perception is the lower spatial resolution of the chromatic system than for chromatic contrast perception, as mentioned in the preceding paragraph.

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28 May 1977

Our goal (*1*) was to compare the explanatory value of two alternative ways of specifying a visual stimulus, rather than to establish the details of possible neural coding mechanisms. As we stated, "The purpose of our experiment is to demonstrate that Fourier analysis can better account for the processing of patterns than an analysis which treats spatial stimuli as collections of visual features."

Smith seems to take it for granted that the visual system must respond to the periodic components of a pattern and that the only trick is to determine their orientations. To this end, he describes a useful informal method of doing so. However, a Fourier analysis is not the only way to describe a scene, since it may also be described as a set of features. The Fourier components of a pattern represent its global attributes, whereas a feature description represents its local attributes. In our study, we had no a priori reason to assume that color aftereffects would be contingent on the inducing checkerboard's global (diagonal) properties rather than on its local (horizontal and vertical) properties.

Tyler shows that it is possible to account for our results if one postulates a neural receptive field structure which "happens to be three or four times larger" than the squares in the checkerboard. This again is an after-the-fact account. Neurophysiological data indicate that visual receptive fields vary widely in size. Prior to experimental testing there is no reason to assume that visual responses produced by checkerboards would be more consistent with the operation of neurons with large, diagonal-sensitive receptive fields than by ones with smaller, edge-sensitive receptive fields.

Tyler suggests that our results can be attributed to the poor spatial resolution of the eye's red-green system. This explanation is unlikely because recent experiments (*2*) with purely achromatic stimuli have demonstrated that detection thresholds for gratings are significantly raised after exposure to checkerboards whose Fourier components are aligned with the gratings, whereas thresholds are only slightly affected by checkerboards whose edges are aligned with the gratings. By Tyler's account, these results would have to be mediated by "large receptive fields in the achromatic channels," but he offers no independent evidence to specify why large rather than small receptive fields should be involved.

Not all stimulus descriptions are equally useful. One value of the Fourier analysis approach to spatial vision lies in its ability to make precise quantitative predictions, which are difficult to make from a feature analysis point of view. Although Fourier analysis may be a complex way to describe a pattern mathematically, it can yield simpler psychophysical relationships than a more straightforward description. The situation is analogous to choosing a coordinate system with which to describe the motion of a particle. From a straightforward rectilinear point of view, polar coordinates are mathematically complex. But if the particle happens to be rotating, polar coordinates provide a simpler description of its known path and its possible future location than rectangular coordinates do. As visual scientists, we prefer simpler psychophysical relationships to simpler stimulus descriptions. Moreover, to the extent that predictions specified by a Fourier analysis of a pattern are verified, we feel justified in concluding that the visual system as a whole responds as if to the Fourier components of the pattern.

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Both Smith and Tyler address the question of whether or not the visual system actually performs Fourier analysis of spatially complex stimuli. We did not feel that our results constituted direct support for such a notion and consequently were quite tentative in our statements about whether patterned information is processed by Fourier analysis as opposed to feature detection mechanisms. We felt that it would be just as premature to attribute perceptual responses to single cortical units as it would be to state that the brain performs Fourier analysis. Our experiments examined perceptual responses as they relate to one of many heuristic methods of describing visual inputs.

With respect to Smith's nonmathematical explanation of the perceptual response to a checkerboard, it is not at all clear how the output of the moving slit is translated into the perceptual phenomena that we described. Tyler's analysis constitutes a description of possible initial stages of perceptual processing. If the brain does perform something analogous to Fourier analysis of visual inputs—a notion which is more directly supported by other studies (*1*)—the interaction of outputs from a large number of single units must be involved. It is perfectly plausible to state that a hypothetical cortical unit *could* show maximal activity when stimulated with the diagonals of a checkerboard, but observations indicating that an orientation-specific single unit *does* respond maximally to the fundamental Fourier components of both gratings and checkerboards would be more impressive. So far as we know, data of this kind have not yet been reported.

Tyler's statement concerning poor spatial resolution in the chromatic channels does not seem to add much to our understanding of these effects, especially given his comment that "large receptive fields could also occur in the achromatic channels." He is correct in predicting achromatic aftereffects. As yet unpublished data from several laboratories indicate that results commensurate with our color aftereffects can be obtained with achromatic stimuli. Threshold elevations, obtained under conditions of successive adaptation (*2*), simultaneous contrast (*3*), and interocular suppression (*4*), occur whenever the major Fourier components of checkerboards and gratings have the same orientation. Using achromatic contrast thresholds and checkerboards with Fourier frequencies as low as two cycles per degree, the aftereffect occurs on the diagonals (*2*). Thus, it seems clear that poor spatial resolution occurs with achromatic aftereffects as well as with chromatic aftereffects.

Fourier analysis has made a considerable contribution to the study of pattern perception. Without this powerful conceptualization the argument discussed here would not have occurred. The contribution of electrophysiological data to the understanding of perception has also been great; however, as this argument indicates, the exact relationships between single-unit responses and psychophysical judgments remain to be specified. Fourier components are essentially a feature of the stimulus; our experiment asked what features were salient in this situation rather than directly addressing the question of the type of mechanisms involved.

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17 June 1976

Simple Solutions: Concentrations in the Surface Region

In an otherwise excellent article on the colligative properties of simple solutions (*1*), Andrews makes some incorrect statements about concentrations of molecules in the surface region between a liquid solution and its equilibrium vapor phase. He states that in an ideal (Raoult's law) solution "solute molecules occupy the same fraction of the surface as their mole fraction" and that in a Henry's law solution "these fractions are not necessarily the same but they are proportional" (*1*, p. 569). Neither of these statements is true in general, although one can imagine particular binary liquid solutions in which (relative) surface concentrations are the same as bulk concentrations.

Numerous adsorption studies have shown that surface concentrations of solutes (in regions where the solute obeys Henry's law and the solvent follows Raoult's law) are decidedly nonlinear in bulk solute concentration. Typically, the concentration of a surface-active solute in the interfacial region will increase to a saturation value (often corresponding nearly to monolayer coverage) at low bulk concentrations and will change very little at much larger solute concentrations or activities. To be sure, the rate of evaporation of a solvent can be considerably reduced by the presence of a monomolecular layer of a slightly soluble compound (*2*); however, the rate of return of solvent molecules to the bulk solution will be simultaneously reduced by (nearly) the same fraction.

The major point is that, although the kinetics of evaporation and condensation are quite complicated, the arguments developed by Andrews can be made (and in fact are made throughout the rest of Andrews's article) solely in terms of the reduction of solvent chemical potential (μ_1) caused by the presence of a dissolved solute. Stated somewhat differently, the kinetics of evaporation and condensation must be consistent with the thermodynamics, but the actual mechanism of these processes and the changes that occur in the molecular composition of the surface region are of little interest in relation to the thermodynamic treatment of colligative properties.

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I thank Christian and Tucker for calling attention to the molecular model I chose to illustrate ideal vapor pressures in one paragraph of my article. I did not make clear the fact that the model I used was simply an example, chosen because it was easy to understand. Their point is well taken that in many cases more complicated models are required to explain the mechanism of these phenomena, although the overriding thermodynamics is thoroughly understood.

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