Alexandrite (Al$_{2-x}$Cr$_x$BeO$_4$), a variety of chrysoberyl, is valued as a gem stone because of its unique optical properties. Its striking and characteristic property is a change from a green color to a reddish purple in different environments. The origin of this color change is often attributed, quite erroneously, to dichroism. Simple observation shows that the change depends chiefly on the nature of the incident light. In antiquity this change was from sunlight to (presumably) candlelight and this exhibition is still used today by many gemologists and jewelers. Striking effects are also observed when the change is from a (blue) fluorescent light to incandescent lighting (low-color temperature). It was this striking color change in a ring when moved from the jewelers’ case to sunlight that drew our attention to this matter. Natural alexandrite is a crystalline solution of Cr$^{3+}$ in Al$_2$BeO$_4$. In general it is not even known what the host structure in the synthetic “alexandrite” is: indeed the manufacturer’s laboratory was not sure whether it was spinel or alumina. This study was aimed at understanding the nature of the crystal field environment giving rise to this rare optical effect. After most of our study was complete, Farrell and Newnham (1965) published the optical spectra of natural and synthetic alexandrite and have shown, as we had, quite clearly that the color and pleochroism are due to the presence of Cr$^{3+}$ in a distorted octahedral site. It is the purpose of this note to add two additional comments to Farrell and Newnham’s interpretation. One is to elucidate further the nature of the visual color change; the second is to point out that such a color-change phenomenon is not a unique property of the mineral alexandrite nor of the Cr$^{3+}$ ion.

Most chromic compounds are either pink or green. In a few series of crystalline solutions, for example, the ruby (Al$_2$O$_3$-Cr$_2$O$_3$) series, the color may be either pink or green depending on the chromium concentration but there has been no report of a color change with change in incident lighting. One should remember that while the energy levels of the Cr$^{3+}$ ion determine the maxima in the absorption spectrum, the observed color is determined chiefly by the minima. Chromic compounds have two such minima, one between the absorption bands and one on the long wavelength end of the spectrum. The wavelengths of the absorption bands are

\[^1\] Also associated with the Department of Geochemistry and Mineralogy.
a function of the strength of the crystal field of the coordination octahe-
dron surrounding the Cr+++ ion. As the field changes, the band positions
and thus the location of the minima shift and the color changes slightly.
The red-green color change in Cr+++ compounds however is more drastic
and not continuous. As is well known, green compounds remain green
with decreasing chromium content until at a critical concentration the
color abruptly becomes pink with only a short range of neutral gray.

Poole (1964) has made a very careful study of the color changes in some
70 chromium compounds by means of tristimulus analysis and has
reached the conclusion that the color change is due to what he calls a
“psycho-physical” effect. That is, the color change is due to the response
of the human eye and brain and not to any abrupt changes in the pro-
erties of the material. As the chromium composition moves from those
values which yield green compounds to those values which yield pink
compounds, the interband minimum in the spectrum moves from near
525 m\(\mu\) toward shorter wavelengths. The eye is very sensitive to green
light and is less sensitive to red and blue so it responds most strongly
to the green light and the compound appears green. As the light passed by
the interband minimum becomes more blue and the light passed by the
long wavelength minimum becomes brighter red, the eye shifts its re-
sponse from predominantly the green stimulus to a mainly red stimulus
with some blue component. The material now appears pink. It appears
certain that the physiological response of the human eye in a particular
part of the visible spectrum is also responsible for the change of color in
alexandrite. We therefore propose the term “Alexandrite Effect” to de-
scribe the phenomenon of an observed color change from greenish to
reddish with a change in source illumination.

Five natural alexandrites (\(Al_2BeO_4\)) were examined. In two of these five
the color-change with incident lighting change was very much more
marked than in the others. Electron probe analysis for the Cr-content
showed that the concentration was near 0.18 mole percent \(Cr_2O_3\) for the
materials showing no change and 0.64 mole percent for those showing a
definite change. The explanation for this must lie in the fact that in order
for the “change” to be observed, the optical absorption must be suffi-
ciently high within the bands not to permit too much transmission “un-
der” the bands.

Moreover, if this general theory of the alexandrite-effect is correct it
should not be a rare phenomenon, and indeed should be observed in many
materials. The most obvious of these, of course, is the \(Al_2O_3-Cr_2O_3\) series
mentioned above, which goes from the characteristic ruby to the bright
green of \(Cr_2O_3\). This behavior has been recently reexamined in some detail
in the ruby \(Cr_2O_3\) series by Barks, Roy and White (1965). The color
change takes place very abruptly near 20 wt. percent \(Cr_2O_3\). The measured
lattice parameters and crystal field parameters were shown to be continuous functions of composition and have no discontinuities whatsoever at the color change point.

Further examination showed that single crystal material with 20 wt. percent $\text{Cr}_2\text{O}_3$ appears distinctly pink when viewed in incandescent light and distinctly green when viewed in daylight. Only rubies with compositions near the critical composition exhibit this effect.

Furthermore, since the alexandrite effect is shown to be due only to critical wavelength minima in the absorption spectrum, there is no reason why this effect should be limited to chromium compounds. Indeed, it is not and one additional example is given here. Many commercial gem mineral supply houses sell what they call synthetic alexandrite. These are typical corundum boules which exhibit an alexandrite-like color change which is even more dramatic than that of most natural stones. Two of these boules were examined. An emission spectrographic analysis is given in Table 1 and the absorption spectrum of the A-boule is given in Figure 1. It is clear therefore that the active element in synthetic “alexandrite” is vanadium, present as $\text{V}^{+++}$. The position of the two absorption peaks agrees well with the bands observed by McClure (1962) and there seems to be little doubt about the assignments. $\text{V}^{+++}$ like $\text{Cr}^{+++}$ has an $F$-ground state and gives rise to three spin-allowed bands, two of which appear in the visible part of the spectrum. The two absorption minima are at 490 and 680 $\text{m\mu}$ compared to Farrell and Newnham’s value of 490 and 670 $\text{m\mu}$ for natural alexandrite. Any ion or combination of ions whose spectrum had minima at these critical values would presumably give a similar effect.

One might ask whether an alexandrite—type color effect could be generated by $\text{Ni}^{++}$ or $\text{Co}^{++}$ in minerals since these ions also have $F$-ground states. The answer is that it is not likely. $\text{V}^{+++}$ and $\text{Cr}^{+++}$ as trivalent ions have crystal field splitting parameters of 1750 and 1815 $\text{cm}^{-1}$ respectively in corundum. $\text{Ni}^{++}$ and $\text{Co}^{++}$ as divalent ions have $Dq$ values of 860 and 1000 $\text{cm}^{-1}$ which reduces the splitting of the energy levels, moves the

<table>
<thead>
<tr>
<th></th>
<th>Crystal A (wt. %)</th>
<th>Crystal B (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}_3\text{O}_5$</td>
<td>1.2</td>
<td>n.d.</td>
</tr>
<tr>
<td>$\text{MnO}$</td>
<td>0.03</td>
<td>n.d.</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td>0.01</td>
<td>n.d.</td>
</tr>
<tr>
<td>$\text{V}_2\text{O}_5$</td>
<td>0.45</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Not detected (n.d.): Co, Ni, Cu, Zn.

Table 1. Emission Spectrographic Analyses of Artificial Alexandrite
absorption bands toward the infrared and makes it very unlikely that the absorption minima could have critical values. Alternatively one could conceive of preparing appropriate mixtures of ions which might permit such a critical window to be generated.

Acknowledgement

Research on the optical spectra of crystals is supported by the National Science Foundation under Grant No. GP-3232.

References

Of all the serpentine minerals, the six-layer ortho-serpentine is least well characterized. It was originally described by Brindley and von Knorring (1954) with additional data given by Zussman, Brindley and Comer (1957), Zussman and Brindley (1957) and by E. Olsen (1963). It has been synthesized by Roy and Roy (1954) and by Gillery (1959). The structure of the mineral is not known and reports on the mode and the frequency of occurrence are scarce. During the investigation of the mineralogical composition of the well-developed serpentinite bodies in Yugoslavia. The mineral was found to be the main constituent of the black serpentinite that occurs as lenses in the Paleozoic schists at Korab Mt. As a pure component it forms thin sheets or lenses interbedded with asbestos veins in the same region. It is inferred from the scarcity of secondary magnetite grains that the rocks prior to serpentinization consisted mainly of high-magnesian olivine. The mineral is a main constituent of a large body of serpentinized dunite at Radusa mine. It is always found in regions where serpentinite rocks have been altered hydrothermally.

**X-Ray Investigation**

Powder data were obtained from a 19 cm. camera using Cu (Ni-filtered) radiation, and fiber photographs were taken in a 6 cm. camera. A fiber photograph of a specimen whose powder pattern is given in column 3 of Table 1, and which is a pure six-layer ortho-serpentine, shows sharp reflexions on all layer lines which are, however, elongated along Debye arcs. On the zero layer line 001, 0k0 and a few 0kl reflexions were