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RELATIONSHIP BETWEEN LIGHT ABSORPTION AND COMPOSITION IN A SOLID SOLUTION SERIES*

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ABSTRACT

Using a spectrophotometer improvised from a monochromator, polarizing microscope, and a photomultiplier tube, light absorbance measurements were made for the γ' direction on a (110) face for crystals of varying nickel content in the solid solution series between $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. Measured absorbance values were found to confirm the Beer-Lambert law within the limits of measurement. On the basis of this law, compositions predicted from absorbance per centimeter values of different crystals were accurate to within 3.0 mol per cent (of the compositions predicted from density values) for 75% of the crystals measured.

Calculations to obviate the effects of opaque inclusions and internal cleavages in the measured crystals when predicting composition from absorbance measurements are discussed.

INTRODUCTION

Previous Investigations

Absorption spectrophotometry rarely has been used to determine the chemical composition of a mixed crystal in a solid solution series; on the other hand, the analysis of liquid solutions by colorimetric methods has found increasing use. To the writer's knowledge Malmqvist (1929, p. 224) was one of the first to realize the possibility of correlating chemical composition and light absorption in a solid solution series and thereby using light absorption measurements to aid in ascertaining the chemical composition of a mixed crystal.

In his work on crystals of varying compositions in the epidote series, Malmqvist attempted to establish for this series the applicability of Beer's law, an expression of the relationship between light absorption and chemical composition in solutions (much used by chemists in the colorimetric analysis of liquids). His conclusion that Beer's law can well be

* An investigation conducted in the laboratories of the Department of Geology of the University of Chicago as part of a Ph.D. thesis by the author.

used for this series (Malmqvist, p. 275) is unfortunately based on all-too-meager data, namely a comparison for two crystals of piedmontite of the amounts of MnO calculated to be present on the basis of: (a) refractive index measurements and (b) absorption measurements at the wavelengths 5893 and 6563 Å.

Tromnau (1934, pp. 355, 368) attempted to determine the relationship between light absorption and chemical composition for some artificial cobalt-colored spinels but, unfortunately, single crystals with sufficient cobalt content to be analyzable proved too opaque whereas crystals sufficiently transparent did not possess enough cobalt for an accurate analysis. In 1936, J. Evers (Rehberg, 1949, p. 1) concluded in an unpublished dissertation that light absorption was a function of chromium content in a series of synthetic spinels but he was unable to determine the nature of this correlation.

One of the first published accounts of a successful confirmation of Beer's law for a solid solution series, that of C. H. Rehberg (1949), became accessible to the writer only after the experimental work of this present paper was well under way. Rehberg performed spectrophotometric measurements on some mixed crystals of the solid solution series between common alum and chrome alum. Using a graphical method of analyzing his data, he found fairly close conformation to Beer's law and further expressed the opinion (1949, p. 18) that Beer's law would probably hold for all solid solutions.

Rehberg's work was excellent but a few points of minor criticism should perhaps be considered: (1) his published graphs were drawn on too small a scale and visual deviations from linearity were thereby suppressed, (2) crystals grown from the same solution were assumed to possess the same composition,* (3) light losses due to reflection were not considered by Rehberg, and (4) the wide (200 Å) spectral band used further reduced accuracy.

In spite of the last three objections, Rehberg's data on absorption enable predictions of composition within an accuracy of 5 mol per cent, if one corrects the typographical errors in his Table 5 (Rehberg, 1949, p. 12) for the 41.9 mol per cent crystal at wavelengths: 540, 560, 580, and 600 μ .

* The present writer found variations of up to 3 mol per cent in the composition of mixed crystals of the same crop when grown by evaporation from aqueous solutions of nickel ammonium sulfate and magnesium ammonium sulfate (under conditions of controlled temperature and humidity). Possibly this effect is not so severe for the chrome-alum crystals used by Rehberg; however, the method of extrapolating an analysis of a sibling crystal to provide the composition of the crystal being spectrophotometrically analyzed introduces undesirable uncertainties.

Selection of the Solid Solution Series to be Studied

Artificially grown mixed crystals of the solid solution series between nickel ammonium sulfate, $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and magnesium ammonium sulfate, $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, were chosen for study because of the following advantages: (1) crystals free of impurities could be obtained, (2) composition of *individual* crystals, as was anticipated, could be accurately predicted (Bloss, 1952, eq. 6) from their densities, and (3) the series was monoclinic and therefore analogous to several important mineral solid solutions to which it is hoped this work may be extended. The first two advantages enumerated were especially helpful in permitting an adequate test of the relationship between light absorption and concentration of colorant without excessive complications.

EXPERIMENTAL DETAILS

A full description of the experimental details appears in an unpublished doctoral dissertation (Bloss, 1951); to orient the reader, however, a synoptic presentation follows.

Growth of Crystals and Determination of Their Composition

The crystals were grown by evaporation (at a controlled temperature and humidity) from saturated aqueous solutions containing nickel ammonium sulfate and magnesium ammonium sulfate in varying proportions. From the previously established equation relating density to composition for this series (Bloss, 1952, p. 970, eq. 6), the composition of small single crystals could be calculated from their density values as measured with a Berman micro-balance. Therefore, the composition of each individual crystal selected for the spectrophotometric work was known with confidence to within one mol per cent (Bloss, 1952, p. 971, Table 4). The measured densities and predicted compositions of the crystals used in the spectrophotometric work are listed in Table 1.

Spectrophotometric Apparatus and Procedures

Arrangement and function of apparatus. A 1000 candle power Pointo-lite bulb, housed at *L* of Fig. 1, served as a source of continuous visible radiation. The collecting lens, *CL*, gathered and focused the light upon the entrance slit, *ES*, of the monochromator, *MO*, which was actually a converted Bausch and Lomb Laboratory Wave-length Spectrometer with a constant deviation prism of the Pellin-Broca type. An empty cooling cell, *CC*, located between *CL* and *ES*, served as a convenient means of controlling light intensity; rotation of the cell about an axis parallel to the brass rod upon which it was mounted altered the percentage of

TABLE 1. COMPOSITION OF CRYSTALS STUDIED

Code Number of Crystal	Density Measurements		Ni(NH ₄) ₂ (SO ₄) ₂ · 6H ₂ O Content of Crystals ^a	
	Average of 3 Determinations	Deviation	Mol Per Cent	Mols Per Liter ^b
0-19	—	—	0.00	0.0000
0-1	1.7512	.0005	15.30	0.7323
0-3	1.7638	.0004	21.61	1.0356
0-9	1.7802	.0001	29.83	1.4318
0-10	1.7824	.0001	30.93	1.4850
0-12	1.8069	.0005	43.14	2.0762
0-11	1.8071	.0001	43.24	2.0810
0-7	1.8537	.0004	66.31	3.2059
0-8	1.8539	.0003	66.41	3.2107
0-17	1.8851	.0010	81.74	3.9640
0-5	1.9013	.0003	89.67	4.3554
0-22	—	—	100.00	4.8671
0-23	—	—	100.00	4.8671

^a With the exception of 0-19, 0-22, and 0-23 which were grown from pure solutions and therefore of known composition, compositions were calculated from the densities using the formula

$$h(\rho) = -1028.0653 + 689.6492\rho - 53.5518\rho^2$$

previously established for this solid solution series (Bloss, 1952, p. 970) to relate composition in terms of mol per cent of Ni(NH₄)₂(SO₄)₂ · 6H₂O as a function, $h(\rho)$, of the crystal's density, ρ .

^b The formula for the conversion of mol per cent to mols per liter is

$$C = \frac{n\rho}{n(N - M) + M}$$

where C represents the mols nickel ammonium sulfate present in a liter volume of a crystal containing n mol per cent nickel ammonium sulfate and having a density of ρ . M and N refer to 360.62 and 394.99 grams, respectively, the gram molecular weights for magnesium ammonium sulfate and nickel ammonium sulfate.

light transmitted through the two parallel glass planes of the cell. After dispersion by MO , the light leaves the exit slit, XS , and is directed upon the substage mirror of the polarizing microscope. By means of the substage lenses, the image of slit XS is focused, now in plane polarized light, into the plane of the microscope stage.

The cable release mount CR , a one-eighth inch thick circular disc of brass with a 0.5 mm. diameter hole at its center (Fig. 2), is screwed onto the microscope stage so that its opening, which acts as a fixed diaphragm, is centered in the field of view of the microscope. Actuation of the cable

release causes *CH*, a removable rectangular piece of brass through which is drilled a 1 mm. diameter hole, to slide centripetally until stopped by the set screw, *SS* (which may be so adjusted that the hole in *CH*, in its arrested position, lies directly over the central hole in *CR*). Upon cessation of pressure on the cable release, *CH* moves centrifugally to a rest position entirely clear of *CR*'s central hole. Thus a crystal mounted on crystal holder, *CH*, can be made to move into or out of the path of a light beam passing through the central hole in *CR*.

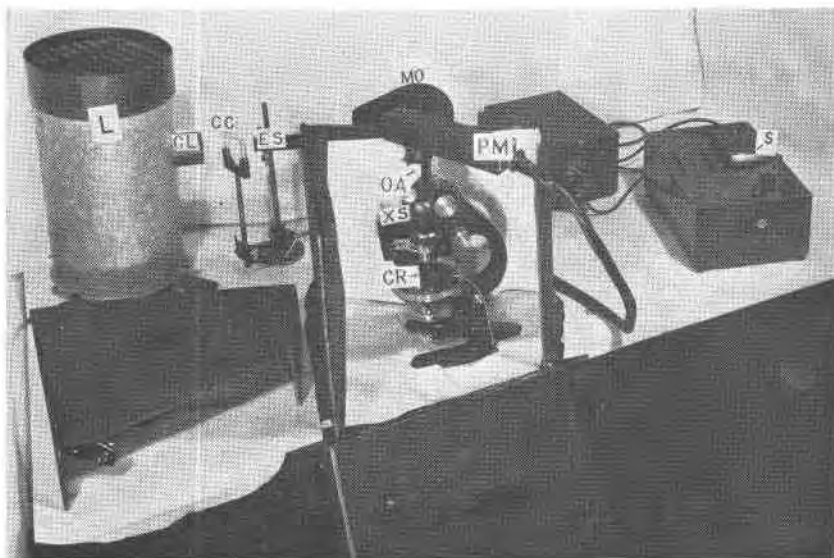


FIG. 1. Arrangement of apparatus for spectrophotometric measurements. For illustrative purposes, the light proof enclosure for the microscope has been opened and pieces of gray paper taped over its dull black finish (and that of the table). Lamp, spectrometer, and microscope were securely fastened to the table to maintain proper alignment. The ordinary substage mirror of the microscope was replaced by a first surface mirror.

Light entering the objective of the microscope follows the usual optical path (analyzer out). The ocular adapter, *OA* of Fig. 1, is essentially a brass tube which fits snugly over the ocular; its upper end is threaded and screws into the housing of the photomultiplier tube, *PM*. Both joints are light tight. Within *OA* a piece of frosted glass is mounted to coincide with the exit pupil. It is essential; without it a light spot at the center of the field of view caused a larger photoelectric response than did a spot of equal area and intensity more peripherally located, an effect probably caused by the curvature of the photomultiplier tube. The intensity of response of the photomultiplier tube to the diffused light from

the frosted glass was read in terms of the arbitrary units of the linearly responding scale, S , of the Photovolt Model 512-M photometer used for this work.

Measurements of light absorption. One of the numbered crystal holders,

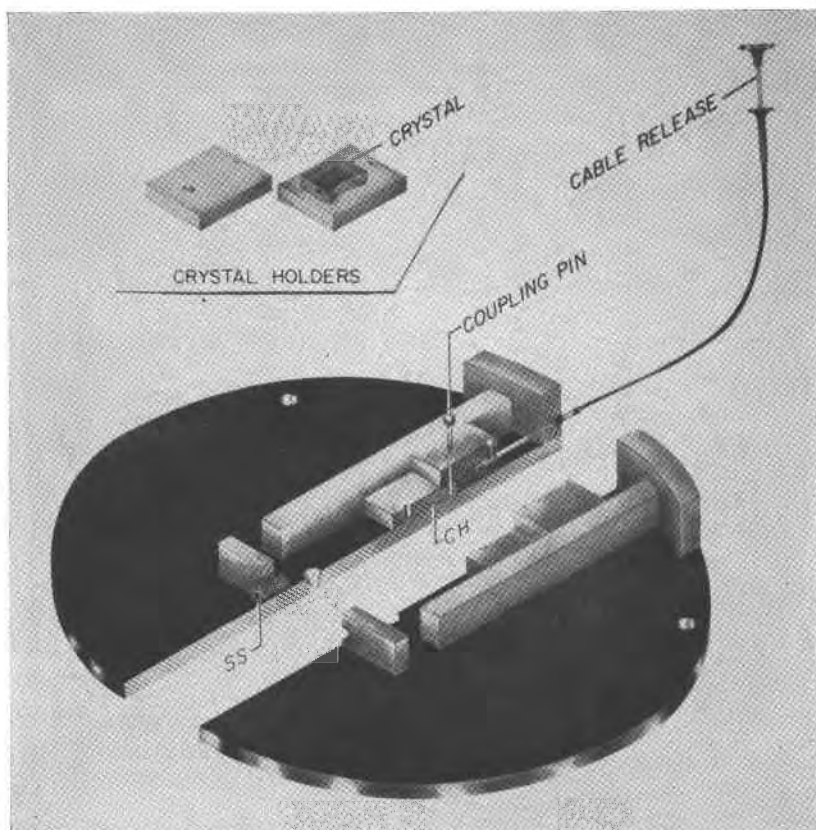


FIG. 2. Isometric sectional view of the cable release mount (CR in Fig. 1). The centrally located, slightly conical hole was 0.5 mm. in diameter (for illustrative purposes both its size and conic shape have been exaggerated); the holes in the crystal holders were 1.0 mm. in diameter. Several extra crystal holders were available and a quick interchange with CH, the crystal holder in place, was possible simply by withdrawing the coupling pin and substituting a crystal holder with a different crystal mounted on it. Two extra crystal holders are shown to the upper left, one with a crystal plate already mounted on it.

CH, upon which a crystal is mounted (Fig. 2), is coupled to the motivating mechanism of the cable release by means of the small coupling pin so that the crystal can be readily moved into or out from the path of the light beam. With the crystal in (nicols crossed, sodium light), the micro-

scope stage is rotated until a minimum reading on scale S indicates an extinction position. With the crystal at the desired extinction position and the analyzer out, the intensity readings on scale S are, for a given wavelength, successively recorded for the crystal inserted into and for it withdrawn from the optical path. Minimization of the interval between insertion and withdrawal decreases the possibility of variation in the intensity of the light source (in response to line voltage fluctuations) between these two readings.

In some instances, however, the intensity fluctuations were so rapid as to inevitably affect the accuracy of the readings. Fortunately the effect was random so that the four or five pairs of readings normally taken for each wavelength generally yielded an average of a higher order of accuracy. Each set of readings was secured as follows: first a reading was taken for the unimpeded beam, next for the crystal-transmitted beam, and lastly for the unimpeded beam again. If the third reading agreed with the first, the results were accepted and the first and second readings were recorded as a pair. Prior, however, to running the series of absorption measurements for the several different wavelengths, the monochromator was set at a wavelength for which the crystal transmitted around 50 to 70 per cent of the light. Set screw SS , Fig. 2, was then adjusted until successive absorption measurements showed a maximum light transmission for a certain position. This was done for each crystal measured so that its clearest portion would always be used.

A second set of observations was often made two or three days later. Eight to ten weeks later some of the crystals were ground to a new thickness and the set of observations was repeated.

Thickness Measurements

After completion of the absorption measurements on a crystal, the thickness of that portion of it over the hole in CH was measured using a micrometer calipers in conjunction with a dial indicator. The dial indicator permitted the same contact pressure to be attained during all measurements. Measurements are believed to be accurate to within .003 cm.

DISCUSSION OF BEER'S LAW

Statement of Beer's Law; Definitions

Beer's law, generally but possibly erroneously believed to have been formulated by Beer (Pfeiffer and Liebhafsky, 1951, p. 123), reads for a solution containing n light-absorbing components through which monochromatic light is transmitted

$$A = \log \frac{I_0}{I} = (\epsilon_a C_a + \epsilon_b C_b + \dots + \epsilon_n C_n) d \quad \text{Eq. (1).}$$

The value $\log I_0/I$ or A is termed absorbance* (Brode, 1950, p. 199); I_0 and I respectively indicate the intensity of the light beam *immediately after entrance into* and *immediately prior to exit from* the solution; C represents the concentration in mols per liter of the respective colorants in the solution; d is the distance in centimeters that the light beam travels through the solution; ϵ represents the molar absorbance of the respective colorants for the light used.

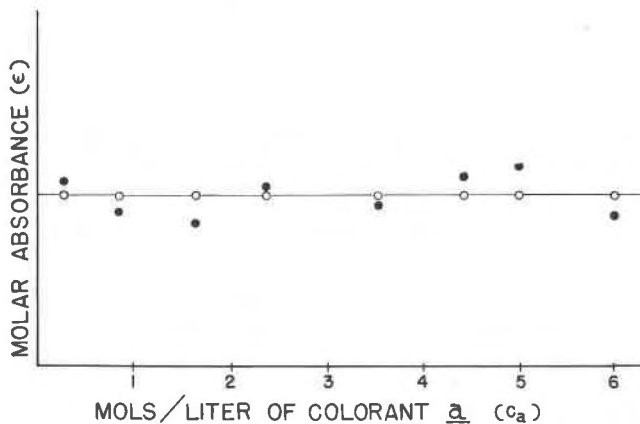


FIG. 3. Hypothetical relationship between molar absorbance (for a given wavelength) and concentration of colorant for eight crystals of a solid solution series between colorant a and a colorless material (monochromatic light assumed). Small circles represent points as would be ideally observed; filled circles represent points when observed with some experimental error.

The value ϵ_a , to be more explicit, represents the absorbance per centimeter of light travel produced by a one-mol-per-liter concentration of colorant a in the solution. In general the value of ϵ differs for different colorants and for different wavelengths of light. For p , a perfectly transparent colorless material, ϵ_p would equal zero for all portions of the visible spectrum. Therefore, for a series of solutions of varying proportions of a perfectly transparent colorless material plus just one particular colorant, Eq. (1) reduces to

$$\text{Log } \frac{I_{0\lambda_1}}{I_{\lambda_1}} = \epsilon_a C_a d \quad \text{Eq. (2)}$$

(for light of wavelength, λ_1).

Method of Statistically Testing Beer's Law

To establish the validity of Beer's law for a series of solutions of a given

* $\text{Log } I_0/I$ is often termed optical density and given the symbol D .

colorant, a , it is necessary to prove that ϵ_a has the same value for all concentrations. Figure 3 graphically expresses such a relationship (hypothetical) for eight different concentrations between colorant a and a colorless solvent; ideally expressed (circles) the data would fall along a perfectly horizontal line. Unfortunately, experimental errors occur and solid circles might better represent the empirical data. Herein arises the necessity for statistical analysis to determine whether the trend of the data deviates sufficiently from parallelism to the abscissa to permit a flat rejection of Beer's law.

By the method of least squares, one can calculate for each particular wavelength the values of the parameters, $\hat{\alpha}$ and $\hat{\beta}$, of the straight line, $\epsilon_a = \hat{\alpha} + \hat{\beta}C_a$, which best follows the trend of the data. If Beer's law is not valid for the series of solutions of colorant a , the value of $\hat{\beta}$ will deviate significantly from zero.

Statistical methods permit the calculation of a certain range to either side of the calculated value, $\hat{\beta}$, to thereby establish an interval around $\hat{\beta}$ within which the true value, β_t , would fall in 19 out of 20 such samplings of the data. This interval, the 0.95 confidence interval,* becomes increasingly confined as experimental accuracy or number of observation increases. The value zero may fall outside of this 0.95 confidence interval, whereupon a rejection of Beer's law would have a 19 out of 20 chance of being the correct choice, or it may fall within this interval, whereupon the chances are 19 out of 20 that Beer's law is valid within the limits of measurement. In the latter event, the possibility still remains that future investigations may, through greater accuracy or larger number of observations, permit calculation of a narrower 0.95 confidence interval which will exclude zero.

EMPIRICAL DATA AND RELATED CALCULATIONS

Preliminary Examinations and Confinement of Data

A crystal of the colorless magnesium-rich end member, $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and of the deep green nickel-rich end member, $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, were each mounted, lying on a (110) face, on a crystal holder. Their absorbance values for the two extinction positions measured for different wavelengths† are graphically expressed in Fig. 4. Conclusions from these preliminary examinations were: (1) the light

* Discussion of confidence intervals and of the statistical quantity t used in its calculation may be found in Snedecor (1946, pp. 41-42, 62-66).

† The spectral band isolated by the monochromator was determined to be approximately 35\AA wide in the region of the sodium doublet; its width varied slightly, however, as other regions in the visible spectrum were isolated. Each spectral band of light used is here designated by the wavelength setting of the monochromator.

absorption by the colorless end member is extremely small for either extinction position, (2) absorption by the green end member is relatively large, especially for the longer wavelengths, (3) the green colors respectively transmitted by the α' and γ' vibration directions of the nickel end member, although visually indistinguishable, are readily differentiated when the absorption curves are compared—an effect for convenience referred to as cryptopleochroism.

Since the absorption curves for the α' and γ' vibration directions were

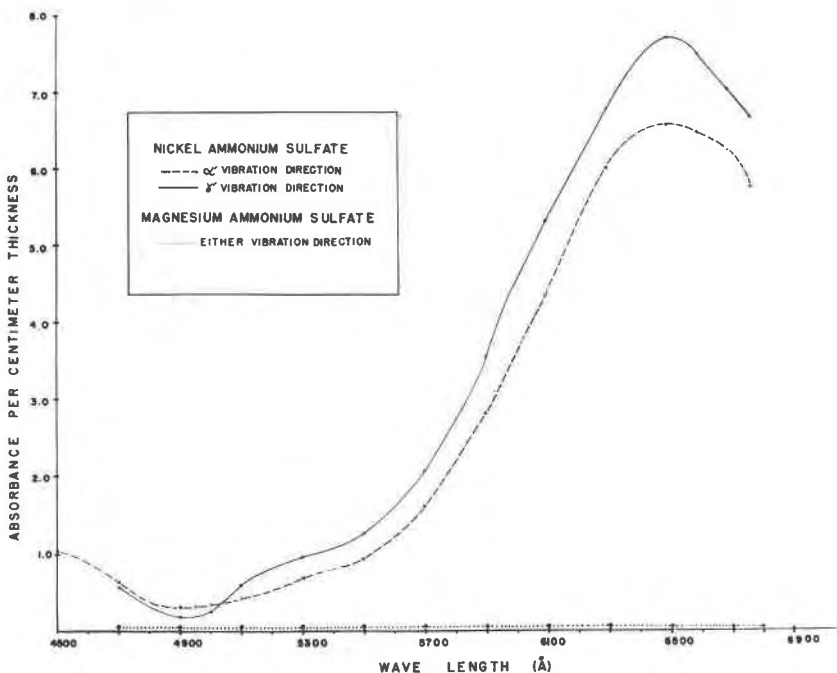


FIG. 4. Absorption curves for α' and γ' directions on a (110) face for nickel ammonium sulfate and for magnesium ammonium sulfate.

so similar (possibly an outgrowth of the almost isometric nature of the internal structure of crystals in this series), the measurements of light absorbance were confined to the γ' vibration direction for those crystals studied.

Compositions of the Crystals Examined Spectrophotometrically

In addition to the preceding two crystals, another crystal of the nickel-rich end member as well as the ten crystals whose compositions were previously stated in Table 1 were examined spectrophotometrically. Several

were ground to new thicknesses and the spectrophotometric measurements were repeated.

Reflectional Losses at Interfaces

If one considers the reflectional losses at the air-crystal and crystal-air interfaces, it is apparent from Fig. 5 that the light intensity values measured as the crystal was slid into and out of the light beam are not I and I_0 as previously defined but rather, I' and I_0' , where

$$I_0 = I_0' - I_0'R \quad \text{and} \quad I' = I - IR$$

and R is the coefficient of reflection for normal incidence. The relation-

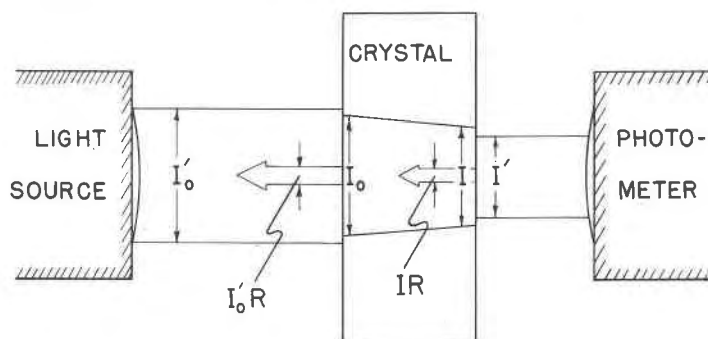


FIG. 5. Relationship between I_0' , I_0 , I , and I' , respectively, the intensity of the light incident upon an absorbing crystal, immediately after entering the crystal, immediately prior to leaving, and immediately after leaving. R represents the coefficient of reflection for normal incidence. Reflection losses at interfaces are shown by arrows pointing left; width of beam or arrow diagrammatically indicates intensity of the light. Photometer measures I' when crystal is in path of light beam, I_0' when it is not.

ship between the observed ratio I_0'/I' and the desired ratio I_0/I is therefore

$$\frac{I_0}{I} = \frac{I_0'}{I'} (1 - R)^2 \quad \text{Eq. (3).}$$

For the crystal series and vibration direction investigated R may be calculated from the basic equation (Wood, 1934, p. 411) to be

$$R = \frac{(\gamma' - 1)^2}{(\gamma' + 1)^2} \quad \text{Eq. (4).}$$

For the two end members the values of γ' and subsequently the values of R were calculated for wavelengths 4700, 4900, 5000, 5100, 5300, 5500, 5700, 5900, 6100, 6300, 6500, 6600, 6700, and 6800 Å using Tutton's (1905, pp. 1136-37; 1916, pp. 7-9) data. The values of R for intermediate

TABLE 2. CORRECTION VALUES $(1 - R)^2$ FOR AIR-CRYSTAL REFLECTION LOSSES (NORMAL INCIDENCE ON (110) FACE)

Crystal	Mol. % Nickel Ammonium Sulfate	Wavelengths (Angstrom Units)														
		4700	4900	5000	5100	5300	5500	5700	5900	6100	6300	6500	6600	6700	6800	
0-19	0.00	0.9270	0.9272	0.9274	0.9276	0.9279	0.9280	0.9282	0.9284	0.9285	0.9287	0.9288	0.9291	0.9292	0.9293	
0-1	15.30	.9259	.9261	.9263	.9265	.9268	.9269	.9271	.9273	.9274	.9276	.9277	.9280	.9280	.9282	
0-3	21.61	.9255	.9257	.9259	.9261	.9264	.9265	.9267	.9269	.9270	.9272	.9273	.9275	.9276	.9277	
0-9	29.83	.9249	.9251	.9253	.9255	.9258	.9259	.9261	.9263	.9264	.9266	.9267	.9269	.9270	.9271	
0-10	30.93	.9249	.9251	.9253	.9255	.9258	.9259	.9261	.9263	.9264	.9266	.9267	.9269	.9270	.9271	
0-12	43.14	.9240	.9242	.9244	.9246	.9249	.9250	.9252	.9254	.9255	.9257	.9258	.9260	.9261	.9262	
0-11	43.24	.9240	.9242	.9244	.9246	.9249	.9250	.9252	.9254	.9255	.9257	.9258	.9260	.9261	.9262	
0-7	66.31	.9226	.9228	.9230	.9232	.9235	.9236	.9238	.9240	.9241	.9243	.9244	.9246	.9247	.9248	
0-8	66.41	.9226	.9228	.9230	.9232	.9235	.9236	.9238	.9240	.9241	.9243	.9244	.9246	.9247	.9248	
0-17	81.74	.9217	.9219	.9221	.9223	.9227	.9227	.9229	.9231	.9232	.9234	.9235	.9237	.9238	.9249	
0-5	89.67	.9212	.9214	.9216	.9218	.9221	.9222	.9224	.9226	.9227	.9229	.9230	.9232	.9233	.9234	
0-22	100.00	0.9204	0.9206	0.9208	0.9210	0.9213	0.9214	0.9216	0.9218	0.9219	0.9220	0.9221	0.9223	0.9224	0.9225	

members in the series were secured, with sufficient accuracy, by interpolation between the end member values.

The computed values of $(1 - R)^2$ for the crystals studied and wavelengths used are given in Table 2.

The Reflection-Corrected Empirical Data

Table 3 presents the empirically determined apparent opacity values, I_0'/I' , multiplied by the pertinent $(1 - R)^2$ values of Table 2; these values

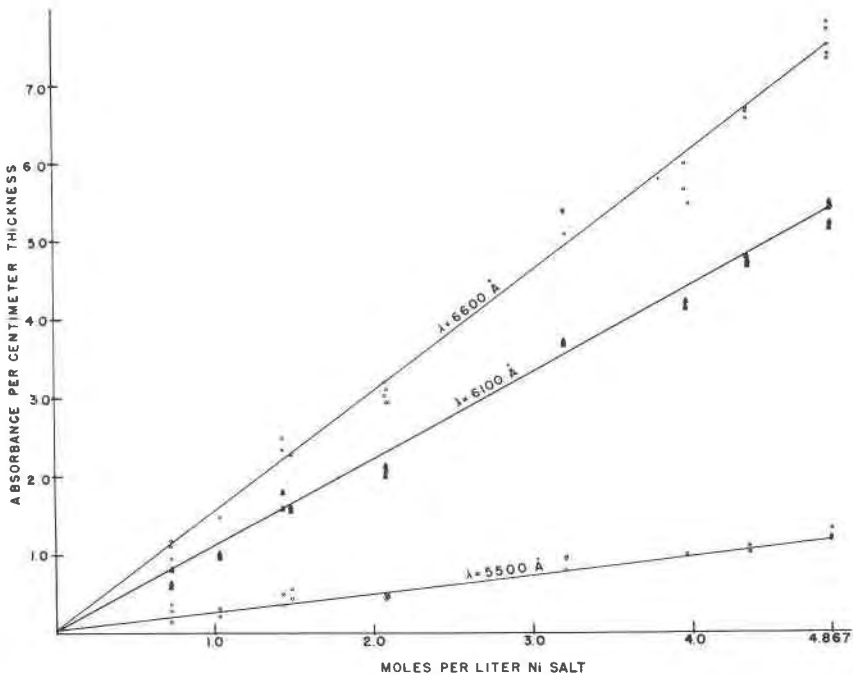


FIG. 6. Absorbance of crystals per centimeter thickness for wavelengths 5500, 6100, and 6600 Å, respectively, plotted against nickel ammonium sulfate content. The straight lines denote the first degree equations of best fit (as determined by the method of least squares).

thus represent the true opacity, I_0/I . Each of the I_0'/I' values upon which they were based represents the average of at least three such ratios; for values where precision seemed below average up to eight or nine I_0'/I' values were obtained and averaged.

Calculation of Absorbance per Centimeter

The logarithm to the base 10 of each value in Table 3 (i.e., the ab-

TABLE 3. REFLECTION-CORRECTED VALUES OF OPACITY* FOR γ' DIRECTION ON (110) FACE

Crystal	Mol % Nickel Ammonium Sulfate	Thick- ness (cm)	Trial	Wavelengths (Angstrom Units)															
				4700	4900	5000	5100	5300	5500	5700	5900	6100	6300	6500	6600	6700	6800		
0-19	0.00	0.347	1	1.04	1.03	1.03	1.02	1.04	1.03	1.03	1.03	1.02	1.02	1.02	1.02	1.02	1.03	1.02	1.02
0-1	15.30	.160 .147	1	1.09	1.10	1.11	1.12	1.13	1.15	1.15	1.16	1.25	1.35	1.50	1.54	1.55	1.58	1.54	1.54
			2	1.08	1.07	1.07	1.08	1.10	1.11	1.31	1.31	1.31	1.44	1.49	1.51	1.48	1.47	1.47	1.47
			3	1.07	1.07	1.00	1.01	1.03	1.04	1.07	1.14	1.14	1.07	1.14	1.24	1.32	1.38	1.38	1.37
0-3	21.61	.184	1	1.09	1.08	1.08	1.09	1.11	1.14	1.14	1.19	1.32	1.54	1.76	1.88	1.88	1.86	1.81	1.81
			2	1.07	1.04	1.06	1.06	1.08	1.10	1.16	1.29	1.51	1.71	1.86	1.89	1.84	1.84	1.76	1.76
0-9	29.83	.210 .190	1	1.08	1.06	1.06	1.09	1.15	1.20	1.20	1.33	1.64	2.16	2.72	3.12	3.12	3.09	2.85	2.85
			2	1.08	1.06	1.12	1.14	1.19	1.25	1.37	1.67	2.20	2.80	3.09	2.98	2.94	2.85	2.85	2.85
0-10	30.93	.185 .170	1	1.24	1.17	1.19	1.20	1.25	1.28	1.28	1.39	1.60	2.00	2.39	2.68	2.66	2.53	2.47	2.47
			2	1.08	1.06	1.07	1.08	1.11	1.15	1.29	1.50	1.84	2.23	2.45	2.44	2.40	2.36	2.36	
0-12	43.14	.121 .111	1	1.07	1.04	1.04	1.07	1.12	1.15	1.15	1.25	1.45	1.79	2.15	2.36	2.44	2.31	2.29	
			2	1.07	1.04	1.06	1.07	1.12	1.15	1.21	1.38	1.67	2.03	2.20	2.18	2.20	2.16	2.16	
0-11	43.24	.134 .129	1	1.07	1.04	1.05	1.07	1.12	1.15	1.15	1.26	1.49	1.89	2.26	2.53	2.49	2.40	2.37	
			2	1.07	1.04	1.06	1.07	1.12	1.15	1.27	1.50	1.88	2.27	2.50	2.52	2.50	2.50	2.50	
0-7	66.31	.131 .120	1	1.17	1.13	1.17	1.18	1.25	1.33	1.55	2.11	3.06	4.29	5.24	5.05	4.90	4.82	4.82	
			2	1.17	1.13	1.08	1.10	1.19	1.28	1.43	1.94	2.77	3.97	4.59	4.42	4.36	4.37	4.37	
0-8	66.41	.164	1	1.18	1.13	1.17	1.19	1.34	1.44	1.74	2.51	3.99	6.19	7.54	6.85	6.58	5.77	5.77	
0-17	81.74	.183 .158	1	1.21	1.14	1.16	1.21	1.36	1.49	1.94	3.19	5.70	9.72	12.14	10.82	9.64	8.41	8.41	
			2	1.21	1.14	1.17	1.23	1.34	1.45	1.81	2.74	4.61	7.70	9.31	8.81	8.09	7.17	7.17	
0-5	89.67	.161 .111	1	1.24	1.16	1.16	1.25	1.39	1.51	1.91	3.04	5.73	9.24	11.08	11.91	10.74	9.15	9.15	
			2	1.25	1.14	1.16	1.22	1.36	1.48	1.89	3.02	5.66	10.00	11.76	11.58	10.00	8.47	8.47	
			3	1.25	1.14	1.10	1.13	1.21	1.30	1.56	2.08	3.39	4.94	5.78	5.46	5.17	4.90	4.90	
0-22	100.00	.144 .102	1	1.20	1.12	1.15	1.19	1.32	1.45	1.84	2.88	4.97	8.95	10.39	9.68	9.13	8.76	8.76	
			2	1.23	1.16	1.19	1.23	1.37	1.51	1.86	2.99	5.38	9.03	13.06	10.95	10.80	9.23	9.23	
			3	1.23	1.16	1.09	1.13	1.23	1.32	1.60	2.28	3.61	5.58	6.18	6.11	5.53	5.42	5.42	
0-23	100.00	.146 0.1235	1	1.21	1.14	1.17	1.23	1.39	1.54	2.00	3.29	5.97	9.69	13.27	12.42	10.62	9.39	9.39	
			2	1.18	1.11	1.14	1.23	1.35	1.49	1.92	3.15	5.60	9.50	10.90	11.63	10.21	8.32	8.32	
			3	1.18	1.11	1.14	1.18	1.31	1.42	1.76	2.65	4.68	7.65	8.84	8.06	8.03	7.37	7.37	

* Each of these values represents the product of the average of at least three to four observed opacity values, I_0/I , times the appropriate reflection correction value, $(1-R)^2$, of Table 5.

sorbance) was next divided by the thickness of the crystal to yield the absorbance per centimeter of the crystal for each of the wavelengths used. Results are given in Table 4. Figures 6 and 7 express the results graphically for several wavelengths.

Calculation of the Molar Absorbance (ϵ_{ni}) for $Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in the Mixed Crystals

A problem encountered in this calculation stemmed from the fact that accurate spectrophotometric measurements could not be made on the

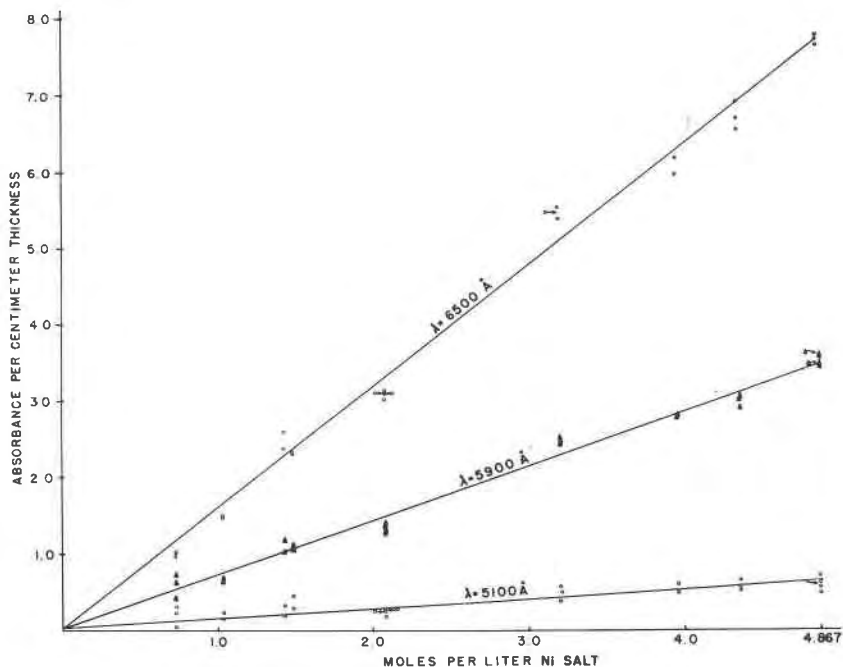


Fig. 7. Absorbance of crystals per centimeter thickness for wavelengths 5100, 5900, and 6500 \AA , respectively, plotted against nickel ammonium sulfate content.

pure, highly transparent $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ crystals since accuracy decreases sharply as complete transparency is approached. The individual absorbance per centimeter values for crystal 0-19 in Table 4 are thus questionable. As a result the amount of absorbance per centimeter contributed by the $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ components of the solid solutions could not be accurately assessed and therefore their ϵ_{ni} values could not be accurately calculated.

Two assumptions were made which are thought to be extremes be-

TABLE 4. ABSORBANCE PER CENTIMETER THICKNESS* FOR γ' DIRECTION ON (110) FACE OF MIXED CRYSTALS OF $(\text{NH}_4)_2(\text{Mg}, \text{Ni})(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

Crystal	Concentration of Nickel Ammonium Sulfate in Crystal		Thick-ness (cm) (4)	Trial (5)	Wavelengths (Angstrom Units)													
	Mol %	Mols per Liter			4700 (6)	4900 (7)	5000 (8)	5100 (9)	5300 (10)	5500 (11)	5700 (12)	5900 (13)	6100 (14)	6300 (15)	6500 (16)	6600 (17)	6700 (18)	6800 (19)
0-19	0.00	0.000	0.347	1	0.048	0.038	0.037	0.030	0.044	0.035	0.035	0.027	0.026	0.019	0.037	0.037	0.025	
0-1	15.30	0.732	1.60	1	.236	.259	.283	.295	.339	.377	.408	.610	.870	1.169	1.186	1.238	1.172	
			.147	3	.216	.184	.181	.211	.251	.283	.370	.733	.780	0.994	1.110	1.059	1.037	
				3	.000	.029	.068	.136	.204	.408	.612	0.816	0.952	0.952	0.952	0.952	0.884	
0-3	21.61	1.036	.184	2	.199	.175	.179	.212	.248	.309	.409	.657	1.022	1.334	1.494	1.465	1.395	
			.184	2	.153	.088	.129	.126	.175	.216	.350	0.607	0.970	1.265	1.458	1.496	1.333	
0-9	29.83	1.432	.210	1	.153	.115	.117	.171	.282	.374	.593	1.021	1.594	2.073	2.356	2.334	2.167	
			.190	2	.259	.259	.300	.398	.510	.720	1.172	1.802	2.354	2.579	2.496	2.465	2.394	
0-10	30.93	1.485	.185	1	.514	.373	.414	.428	.516	.574	.773	1.105	1.624	2.042	2.296	2.180	2.119	
			.170	2	.244	.267	.244	.267	.357	.445	.651	1.036	1.558	2.049	2.279	2.236	2.194	
0-12	43.14	2.076	.121	1	.286	.209	.246	.260	.362	.495	.787	1.334	2.080	2.741	3.207	3.010	2.968	
			.111	2	.153	.227	.153	.227	.335	.441	.743	1.255	1.997	2.758	3.071	3.071	3.000	
0-11	43.24	2.081	.134	1	.210	.140	.158	.222	.359	.459	.746	1.286	2.055	2.641	3.002	2.953	2.798	
			.129	2	.196	.408	.196	.228	.412	.500	.805	1.365	2.126	2.760	3.112	3.085	3.085	
0-7	66.31	3.206	.131	1	.521	.405	.521	.543	.742	.955	1.451	2.475	3.711	4.827	5.492	5.265	5.213	
			.120	2	.278	.278	.345	.630	.808	1.345	2.398	3.688	4.990	5.515	5.378	5.329	5.338	
0-8	66.41	3.221	.164	1	.447	.312	.413	.461	.765	.966	1.471	2.440	3.664	4.828	5.350	4.988	4.639	
0-17	81.74	3.964	.183	1	.450	.309	.356	.450	.723	.814	1.576	2.750	4.131	5.396	5.652	5.378	5.054	
			.158	2	.408	.408	.408	.569	.804	1.022	1.631	2.771	4.201	5.981	5.747	5.415	5.415	
0-5	89.67	4.355	.161	1	.582	.391	.403	.611	.879	1.110	1.743	2.998	4.709	5.997	6.487	6.405	5.972	
			.111	3	.595	.346	.373	.478	.821	1.048	1.720	2.978	4.673	6.208	6.645	6.207	6.559	
				3	.365	.365	.365	.518	.746	1.026	1.740	2.866	4.777	6.250	6.864	6.641	6.428	
0-22	100.00	4.867	.134	1	.580	.359	.439	.569	0.905	1.200	1.980	3.427	5.199	7.102	7.586	7.169	7.033	
			.102	3	.663	.473	.553	.666	1.018	1.327	2.013	3.549	5.455	7.132	8.328	7.757	7.204	
				3	.365	.365	.365	.518	0.877	1.177	1.991	3.492	5.439	7.284	7.717	7.668	7.161	
0-23	100.00	4.867	.146	1	.572	.392	.464	.604	.969	1.275	2.065	3.545	5.314	7.691	7.494	7.027	6.663	
			0.123	3	0.495	0.310	.382	.621	.886	1.176	1.939	3.410	5.126	6.695	7.104	7.298	6.912	
				3	0.461	0.382	0.461	.604	.950	1.233	1.988	3.428	5.427	7.156	7.663	7.326	7.024	

* These values are secured through division of the logarithm of the corresponding value in Table 6 by the thickness in centimeters of the crystal in question, i.e., $\frac{A}{d} = \frac{1}{d} \log \frac{I_0}{I}$

tween which the actual situation lies: (a) the $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ portions of these crystals absorbed no light, (b) their absorbance per centimeter value is 0.033, i. e. the arithmetic mean of the values for all wave-

TABLE 5. CALCULATED VALUES OF ϵ_{ni} THE MOLAR ABSORBANCE OF $Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$ AT SEVERAL WAVELENGTHS (UNDER THE ASSUMPTION THAT E_{mg} , THE MOLAR ABSORBANCE OF $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$, EQUALS ZERO)

Crystal	Trial	Wavelength in Angstroms								
		5500	5700	5900	6100	6300	6500	6600	6700	6800
0-1	(1)	.515	.557	.833	1.116	1.493	1.597	1.620	1.691	1.601
	(2)	.387	.505	1.001	1.066	1.358	1.478	1.516	1.447	1.417
	(3)	.186	.279	.557	.836	1.115	1.301	1.301	1.301	1.208
0-3	(1)	.298	.395	.634	.986	1.288	1.442	1.438	1.414	1.347
	(2)	.208	.338	.586	.936	1.221	1.407	1.444	1.393	1.287
0-9	(1)	.261	.414	.713	1.113	1.448	1.645	1.644	1.630	1.513
	(2)	.356	.503	.818	1.258	1.644	1.801	1.743	1.721	1.672
0-10	(1)	.387	.521	.744	1.094	1.375	1.557	1.546	1.468	1.427
	(2)	.300	.438	.698	1.049	1.380	1.541	1.535	1.506	1.477
0-12	(1)	.238	.379	.643	1.002	1.320	1.482	1.545	1.450	1.430
	(2)	.212	.358	.605	.962	1.329	1.479	1.462	1.479	1.445
0-11	(1)	.221	.358	.618	.988	1.269	1.443	1.419	1.365	1.345
	(2)	.240	.387	.656	1.022	1.326	1.482	1.495	1.482	1.482
0-17	(1)	.205	.398	.694	1.042	1.361	1.494	1.426	1.357	1.275
	(2)	.258	.411	.699	1.060	1.415	1.547	1.509	1.450	1.366
0-5	(1)	.355	.400	.688	1.081	1.377	1.490	1.135	1.471	1.371
	(2)	.241	.395	.684	1.073	1.425	1.526	1.505	1.425	1.322
	(3)	.236	.400	.658	1.097	1.435	1.576	1.525	1.476	1.428
0-22	(1)	.247	.407	.704	1.068	1.459	1.559	1.512	1.473	1.445
	(2)	.273	.414	.724	1.121	1.465	1.711	1.594	1.585	1.480
	(3)	.242	.409	.717	1.118	1.497	1.586	1.576	1.489	1.471
0-23	(1)	.262	.424	.728	1.092	1.388	1.580	1.540	1.444	1.369
	(2)	.242	.398	.701	1.053	1.376	1.460	1.499	1.420	1.295
	(3)	.253	.408	.704	1.115	1.470	1.574	1.560	1.505	1.443
Av. Value ϵ_{ni}		.273	.415	.706	1.065	1.399	1.549	1.533	1.491	1.430
Av. Value ϵ_{ni} for 0-22, 0-23		.253	.410	.715	1.095	1.443	1.578	1.547	1.486	1.417

lengths given for crystal 0-19 in Table 4. The first is of course a low estimate, the second is possibly high, perhaps produced by small unnoticed flaws in 0-19. It was decided therefore to calculate two sets of ϵ_{ni} values, one for each of the assumptions.

TABLE 6. CALCULATED VALUES OF ϵ_{ni} THE MOLAR ABSORBANCE OF $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ AT SEVERAL WAVELENGTHS (UNDER THE ASSUMPTION THAT ϵ_{mg} , THE MOLAR ABSORBANCE OF $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, EQUALS 0.007 FOR ALL WAVELENGTHS

Crystal	Trial	Wavelength in Angstroms								
		5500	5700	5900	6100	6300	6500	6600	6700	6800
0-1	(1)	0.477	0.519	0.795	1.078	1.455	1.559	1.582	1.653	1.563
	(2)	.348	.467	.963	1.027	1.320	1.440	1.478	1.408	1.378
	(3)	.148	.240	.519	.798	1.077	1.262	1.262	1.262	1.169
0-3	(1)	.273	.370	.609	.961	1.263	1.417	1.413	1.389	1.321
	(2)	.183	.313	.561	.911	1.196	1.382	1.419	1.368	1.262
0-9	(1)	.245	.398	.697	1.097	1.431	1.629	1.628	1.614	1.497
	(2)	.340	.487	.802	1.242	1.628	1.785	1.727	1.705	1.656
0-10	(1)	.371	.505	.729	1.078	1.360	1.541	1.531	1.452	1.411
	(2)	.284	.423	.682	1.034	1.364	1.526	1.519	1.490	1.462
0-12	(1)	.229	.370	.633	.993	1.311	1.473	1.536	1.441	1.421
	(2)	.203	.349	.595	.953	1.319	1.470	1.453	1.470	1.436
0-11	(1)	.211	.349	.609	.978	1.260	1.433	1.410	1.356	1.335
	(2)	.231	.378	.647	1.012	1.317	1.473	1.486	1.473	1.473
0-17	(1)	.204	.396	.692	1.041	1.360	1.493	1.424	1.355	1.273
	(2)	.256	.410	.698	1.058	1.414	1.546	1.507	1.448	1.365
0-5	(1)	.254	.400	.688	1.081	1.376	1.489	1.534	1.470	1.371
	(2)	.240	.394	.683	1.072	1.425	1.525	1.504	1.425	1.322
	(3)	.235	.399	.657	1.096	1.434	1.575	1.524	1.475	1.427
0-22	(1)	.247	.407	.704	1.068	1.459	1.559	1.512	1.473	1.445
	(2)	.273	.414	.729	1.121	1.465	1.711	1.594	1.585	1.480
	(3)	.242	.409	.717	1.118	1.497	1.586	1.576	1.489	1.471
0-23	(1)	.262	.424	.728	1.092	1.388	1.580	1.540	1.444	1.369
	(2)	.242	.398	.701	1.053	1.376	1.460	1.499	1.420	1.295
	(3)	0.253	0.408	0.704	1.115	1.470	1.574	1.560	1.505	1.443
Av. Value of ϵ_{ni}		0.260	0.401	.689	1.045	1.374	1.520	1.509	1.465	1.402
Av. Value of ϵ_{ni} for 0-22-23		0.253	0.410	0.714	1.094	1.442	1.578	1.547	1.486	1.417

Calculation of ϵ_{ni} Assuming $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ Is Perfectly Transparent

Under this assumption the values of ϵ_{ni} at the several wavelengths were determined by dividing the values of Table 4 by the concentration of $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (in mols per liter) for that particular crystal. The results of these calculations are presented in Table 5.

Calculation of ϵ_{ni} Assuming Absorbance per Centimeter for $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ is 0.033.

Assuming A/d for pure $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ to be 0.033 and calculating C_{mg} for the pure end member to be 4.773 mols per liter, then from Eq. (2)

$$\epsilon_{mg} = \frac{\frac{A}{d}}{C_{mg}} = \frac{0.033}{4.773} = 0.007 \quad \text{Eq. (5)}$$

To compute ϵ_{ni} values under the above assumption, Beer's law is written as for a two color component series, i. e.,

$$\frac{A}{d} = \epsilon_{mg}C_{mg} + \epsilon_{ni} C_{ni} = .007C_{mg} + \epsilon_{ni} C_{ni}$$

which becomes if solved for ϵ_{ni}

$$\epsilon_{ni} = \frac{\frac{A}{d} - .007 C_{mg}}{C_{ni}} \quad \text{Eq. (6)}$$

The quantity A/d , of course, merely represents the absorbance per centimeter values of Table 4. Thus if C_{mg} is calculated for each of the solid solutions and since C_{ni} is already known, the values for ϵ_{ni} were then calculable. The values thus calculated appear in Table 6.

TESTING THE DATA WITH RESPECT TO BEER'S LAW

There now remained the necessity of statistically fitting a straight line to the data of both Table 5 and Table 6 to determine whether the slope of the trend line for the data would be zero (if graphed like the hypothetical example in Fig. 3). The general equation for the line could be written

$$\epsilon_{ni} = \hat{\alpha} + \hat{\beta}C_{ni} \quad \text{Eq. (7)}$$

As was previously discussed the value of $\hat{\beta}$ should equal zero or closely approach it, if Beer's law holds for this solid solution series.

Accordingly, the values of $\hat{\alpha}$ and $\hat{\beta}$ were calculated by the method of least squares using the data of both Tables 5 and 6. The regressions† carried out were in terms of ϵ_{ni} values upon C_{ni} , i. e., the lines were fitted under the assumption that C_{ni} was the independent variable, ϵ_{ni} , the dependent variable. Table 7 presents the results of these statistical calculations.

* † In statistical terminology regression signifies the process of fitting a line to the data which accurately follows their trend yet, at least in part, lacks their chance errors.

TABLE 7. SUMMARY OF STATISTICALLY DERIVED VALUES OF PARAMETERS $\hat{\alpha}$ AND $\hat{\beta}$

	Regression of ϵ_{ni} Values (of Table 5) on Composition					Regression of ϵ_{ni} Values (of Table 6) on Composition				
	$\hat{\alpha}$	$\hat{\beta}$	Standard Error of $\hat{\beta}$	Standard Error of $\hat{\beta}$ times t^a	Interval ^b in which β_t is likely to fall	$\hat{\alpha}$	$\hat{\beta}$	Standard Error of β	Standard Error of β times t	Interval ^b in which β_t is likely to fall
5500	.322	-.0174	.0086	.0178	+ .004 to -.0352	.290	-.0105	.0084	.0174	+ .0069 to -.0279
5700	.431	-.0064	.0075	.0155	+ .0091 to -.0219	.396	+ .0017	.0075	.0155	+ .0172 to -.0138
5900	.712	-.0041	.0115	.0238	+ .0197 to -.0353	.681	+ .0029	.0112	.0232	+ .0261 to -.0203
6100	1.010	+ .0161	.0098	.0203	+ .0364 to -.0042	.979	+ .0231	.0099	.0205	+ .0436 to +.0026
6300	1.318	+ .0233	.0125	.0259	+ .0492 to -.0026	1.287	+ .0304	.0126	.0261	+ .0565 to +.0043
6500	1.488	-.0154	.0125	.0259	+ .0413 to -.0105	1.456	+ .0224	.0127	.0263	+ .0487 to -.0039
6600	1.505	+ .0053	.0183	.0379	+ .0432 to -.0326	1.474	+ .0122	.0112	.0232	+ .0354 to -.0110
6700	1.494	-.0060	.0125	.0259	+ .0199 to -.0319	1.462	+ .0011	.0126	.0261	+ .0272 to -.0250
6800	1.441	-.0096	.0147	.0311	+ .0215 to -.0407	0.409	-.0025	.0133	.0275	+ .0250 to -.0300

^a The statistical quantity t refers to "student's" t distribution (Mood, 1950, p. 206; Rider, 1939, pp. 88-98).

^b This is actually the 0.95 confidence interval which will generally, for 19 out of 20 such collections of data, embrace the true value, β_t . The possibility still remains that in 1 out of 20 times, a capricious distribution of the data might occur such that the calculated confidence interval actually would not embrace the value β_t .

Salient points of Table 7 are: (1) the $\hat{\beta}$ values of the left hand column differ from the corresponding ones of the right hand column by .007, the assumed value of ϵ_{ng} , (2) the values of $\hat{\beta}$ are in all cases very small and with two exceptions, never differ from zero by more than t times their standard error (the 0.95 confidence interval).

The first of the above points had been anticipated; if $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ actually absorbed appreciable light (but was assumed to absorb none at all) the result would be that for crystals almost pure with respect to Mg but very low in Ni, ϵ_{ni} would be calculated high by the amount, ϵ_{mg} . For crystals increasingly higher in Ni this discrepancy would decrease so that it vanished for pure $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystals. Thus the line $\epsilon_{\text{ni}} = \hat{\alpha} + \hat{\beta} C_{\text{ni}}$ would automatically be given a negative slope equal to $-\epsilon_{\text{mg}}$ (i. e. $\hat{\beta} = -\epsilon_{\text{mg}}$).

The consistency of this difference between the $\hat{\beta}$ values in the right and left hand columns of Table 7 served as a check on the accuracy of the statistical calculations.

The second of the salient points of Table 7 permits the conclusion that the light absorption data substantiate the validity of Beer's law for this solid solution series (within the limits of measurement). In view of the small sample size, the two exceptions out of 18 samplings are not disturbing; in fact this ratio is not much different from the 1 misleading sample out of 20 which is expectable according to statistical theory (for a 0.95 confidence interval).

APPLICATIONS

Determination of Composition from Light Absorbance

For clear crystals of a solid solution series to which Beer's law is applicable, general equation (1) may be applied; the molar absorbance values, i. e., ϵ values, may be determined from measurements of the absorbance per centimeter values, A/d , of as many crystals of known composition as there are color-producing components in the series. Substitution of this data in eq. (1) yields a set of equations which may be solved simultaneously to determine the molar absorbance values ϵ_a, ϵ_b , etc., of the various colorants involved. With these molar absorbance values established for the specific colorants and light wavelengths used, the compositions of unknown crystals of the series can be determined if their absorbance per centimeter values are measured for as many wavelengths as there are possible colorants.

The above methods of calculation, however, assume the absence of any opaque inclusions, bubbles, internal cleavages, or other flawed areas in the crystal. Obviously, such flawed areas would cause a crystal to intercept a larger amount of light than if it were perfectly clear. Therefore if eq. 1 were directly applied as previously suggested, the crystal's composition would be calculated to have greater amounts of the light absorbing components than it actually had.

This difficulty can be overcome if the usually tenable assumption can

be made that the flawed areas block off essentially the same fraction of light, i.e., k , regardless of light wavelength used. Under this assumption the apparent opacity I_0'/I' would be related to the true opacity I_0/I by the equation

$$\frac{I_0'}{I'} = \frac{I_0}{I(1-k)(1-R)^2} \quad \text{Eq. (8).}$$

The apparent and true absorbance values, A' and A , respectively, would therefore be related as follows

$$A' = A - \log(1-k) - 2 \log(1-R) \quad \text{Eq. (9).}$$

Since for different wavelengths of light the value of $\log(1-k)$ and of $\log(1-R)$ changes but slightly, the difference between the apparent absorbance at two different wavelengths, i.e., $A_{\lambda_1}' - A_{\lambda_2}'$, equals the difference between the true absorbance, $A_{\lambda_1} - A_{\lambda_2}$, at those wavelengths. As a result a "difference" version of eq. 1 may be written

$$A_{\lambda_1}' - A_{\lambda_2}' = (\epsilon_{a\lambda_1} - \epsilon_{a\lambda_2})C_a + (\epsilon_{b\lambda_1} - \epsilon_{b\lambda_2})C_b + \dots \quad \text{Eq. (10)}$$

and used for turbid or flawed crystals just as eq. 1 was used for clear crystals. Numerous *colored* inclusions in the crystal area examined spectrophotometrically would, of course, produce erroneous results by either method of calculation.

Empirical Results for the Series Studied

When light absorbance per centimeter values are established for several crystals of known composition in a solid solution series, it is possible to fit a first degree equation to these values by the method of least squares. If the intent in deriving the equation is to predict a crystal's absorbance per centimeter when its composition is known, absorbance per centimeter should be treated as the dependent variable, composition as the independent variable. For the nickel-magnesium ammonium sulfate crystals studied, an equation of the form

$$\frac{A}{d} = f(C_{ni}) = \hat{\alpha} + \hat{\beta}C_{ni} \quad \text{Eq. (11)}$$

would therefore be secured. The values of the constants $\hat{\alpha}$ and $\hat{\beta}$ are secured for each wavelength's data by the least square calculations. The values of ϵ_{ni} and ϵ_{mg} are calculated to be, for a particular wavelength (or spectral band),

$$\epsilon_{ni} = \frac{\hat{\alpha}}{4.867} + \hat{\beta} \quad \text{Eq. (12)}$$

and

$$\epsilon_{mg} = \frac{\hat{\alpha}}{4.773} \quad \text{Eq. (13)}$$

where 4.867 represents the C_{ni} value of the pure nickel end member and 4.773 represents the C_{mg} value for the pure magnesium end member.

However, if the intent in deriving the equations is to predict composition from measured absorbance data, it is statistically preferable (though less natural) to regard absorbance per centimeter as the independent variable and composition as the dependent variable. The form of the derived equation for the data at each wavelength would be

$$C_{\text{ni}} = f\left(\frac{A}{d}\right) = \hat{\alpha} + \hat{\beta} \frac{A}{d} \quad \text{Eq. (14).}$$

Thus, when the values of the constants $\hat{\alpha}$ and $\hat{\beta}$ have been calculated, the compositions of unknown crystals may be predicted, (in terms of mols of nickel ammonium sulfate per liter of crystal volume) from their measured A/d values.

This second method was applied to the data of Table 4 for the A/d values measured at the 5900 Å, 6500 Å, and 6600 Å wavelengths* and the following equations were derived:

$$C_{\text{ni}} = -0.0047 + 1.4157 \frac{A_{5900}}{d} \quad \text{Eq. (15)}$$

$$C_{\text{ni}} = 0.0188 + 0.6324 \frac{A_{6500}}{d} \quad \text{Eq. (16)}$$

and

$$C_{\text{ni}} = -0.0056 + 0.6491 \frac{A_{6600}}{d} \quad \text{Eq. (17).}$$

In a similar manner equations were fitted to the difference between the A/d values of Table 4 for wavelengths 6500 and 5900 Å, 6600 and 5900 Å, and 6600 and 5000 Å. The following equations based on the "differential absorption" between two different wavelength bands were thereby secured and theoretically should obviate the effects of flaws and turbid areas in the crystal:

$$C_{\text{ni}} = 0.0505 + 1.1359 \frac{A_{6500} - A_{5900}}{d} \quad \text{Eq. (18)}$$

$$C_{\text{ni}} = 0.8190 + 1.1921 \frac{A_{6600} - A_{5900}}{d} \quad \text{Eq. (19)}$$

$$C_{\text{ni}} = 0.0368 + 0.6857 \frac{A_{6600} - A_{5000}}{d} \quad \text{Eq. (20).}$$

By way of statistical comparison of equations 15–20, the residual sum of the squares for each were calculated to be 0.830, 0.786, 0.458, 1.511,

* Actually spectral bands of approximately 35 Å width centered at these wavelengths were used.

TABLE 8

Crystal	Mol %*	Trial	Deviations in Mol Per Cent of Compositions Predicted By Substitution of Absorption Measurements of Table 4 into Eqs. 15-20.							
			Substitution of $\frac{A_\lambda}{d}$ Values				Substitution of $\frac{A_{\lambda_1} - A_{\lambda_2}}{d}$ Values			
			Eq. 15, A_{5500} d	Eq. 16, A_{6500} d	Eq. 17, A_{6000} d	Algebraic Average	Eq. 18, $A_{6500} - A_{5500}$ d	Eq. 19, $A_{6000} - A_{5000}$ d	Eq. 20, $A_{6000} - A_{5000}$ d	Algebraic Average
0-19	0.00	(1)	0.68	0.64	0.39	0.57	0.86	0.35	0.76	0.66
0-1	15.30	(1)	2.55	0.53	0.66	0.10	-0.95	-0.82	-1.56	-2.21
		(2)	6.18	-0.60	-0.35		-5.86	-5.69	-1.19	
		(3)	-3.27	-2.28	-2.47		-1.32	-1.60	-0.86	
0-3	21.61	(1)	-2.28	-1.48	-1.52	-2.07	-0.72	-0.78	-2.06	-0.77
		(2)	-3.74	-1.95	-1.46		-0.39	0.60	-1.27	
0-9	29.83	(1)	0.18	1.58	1.85	2.73	2.77	3.33	2.86	3.23
		(2)	4.56	4.48	3.74		4.46	3.10	2.86	
0-10	30.93	(1)	3.60	-0.08	0.00	0.40	-1.29	-1.23	-3.25	-1.18
		(2)	-0.47	-0.39	0.23		-0.23	0.04	-1.09	
0-12	43.14	(1)	-3.95	-2.30	0.00	-2.86	-0.97	3.33	-0.18	0.49
		(2)	-6.25	-2.36	-2.28		0.97	1.07	-1.27	
0-11	43.24	(1)	-5.45	-3.37	-3.49	-3.18	-1.66	-1.83	-2.63	-1.41
		(2)	-3.14	-2.28	-1.38		-1.58	0.14	-0.92	
0-7	66.31	(1)	6.02	5.88	5.61	5.55	5.59	5.12	3.19	5.96
		(2)	3.86	6.17	5.73		7.91	7.21	6.74	
0-8	66.41	(1)	4.91	3.93	1.87	3.57	2.98	-0.82	0.76	0.97
0-17	81.74	(1)	-1.56	-4.09	-6.19	-2.66	-6.33	-10.25	-6.08	-4.91
		(2)	-0.95	-1.38	-1.81		-1.94	-2.71	-2.18	
0-5	89.67	(1)	-2.36	-4.81	-0.47	-2.52	-7.00	0.84	-0.25	-0.63
		(2)	-2.96	-2.76	-2.18		-2.86	-1.77	-2.14	
		(3)	-6.21	0.10	-1.03		4.87	3.08	-0.41	
0-22	100.00	(1)	-0.41	-1.05	-1.99	1.77	-1.89	-3.62	-1.77	1.82
		(2)	3.14	8.59	3.33		12.58	3.16	2.26	
		(3)	1.48	0.66	2.14		-0.35	2.38	3.66	
0-23	100.00	(1)	3.02	0.31	-0.18	-0.80	-2.20	-3.16	-0.18	-2.40
		(2)	-0.90	-7.32	-2.79		-12.74	-4.66	-1.81	
		(3)	-0.39	-0.04	1.11		-0.14	2.08	1.21	

* Of $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in crystals as calculated from density.

0.819, and 0.443, respectively. From this it can be seen that the empirical data deviate least from equations 17 and 20, most from equation 18.

The relative accuracy of equations 15-20 in predicting composition from light absorbance measurements for this series is indicated in Table

8; for each equation the composition in mols per liter of nickel ammonium sulfate, i.e., C_{ni} was calculated by substituting into it the A/d values of Table 4 (or their differences in the case of equations 18–20). The deviation of the values thereby secured from either the known or density-calculated composition values† is given in terms of mol per cent of the nickel end member. Whereas individual calculations indicated discrepancies up to 12.74 mol per cent, algebraic averages for several calculations were within 3 mol per cent of the density-calculated composition in over 75% of the cases.

These deviations have several possible explanations. Positive devia-

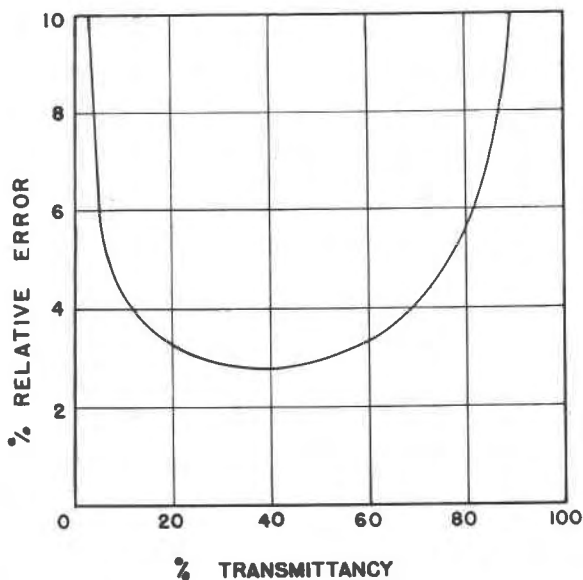


FIG. 8. Relative analysis error as a function of transmittancy (Ayres, 1949, p. 652). Note how relative error increases greatly for crystals with very high or very low transmittancy.

tions from the density-calculated composition may have been caused by opacities or internal reflections in the crystal or by the grinding off during preparation of the crystal (but after the density measurement) of less dense, more transparent, magnesium-rich outer zones. Random deviations could be caused by photometric errors such as nonlinearity in response of the spectrophotometer, fluctuation in intensity of light source, or by errors in reading the scale.

In general photometric errors cause a relatively greater error in pre-

† For crystals of this series the density calculated values are likely to be within 1 mol per cent of the analyzed values (see Bloss, 1952, Table 4).

diction of composition for crystals outside the 20 to 60% transmittancy ($= I/I_0$) range (Fig. 8); theoretically the relative error is at a minimum for transmittancies of about 36.8%. However, even for crystals of thicknesses and color concentrations such that they transmit 36.8% of the light, an error of 1 division in the photometer scale reading would result in a concentration error of about 2.7% of the actual value. (Ayres, 1949, p. 652). Table 8 should thus show greatest deviations for the nickel-rich crystals since transmittancy was occasionally around 70 to 90%. This trend does seem to exist but, by the same token, the later trials at lesser thicknesses for these crystals should yield increasingly accurate results as the 20 to 60% transmittancy range is approached or attained (assuming the crystals are not zoned), an effect which is not apparent.

For eqs. 18 and 19 the "absorption difference" method of calculation proved rather unsuccessful, perhaps because the difference in absorption between the wavelengths involved was not as large as for the more successful eq. 20. (As this absorbance difference decreases, the $\hat{\beta}$ parameter necessarily becomes larger in value and this, in turn, may serve to magnify the effect of random photometric errors.) Eq. 20 did exhibit a superiority which was definite with respect to equations 15 and 16, but only slight with respect to equation 17.

CONCLUSIONS

1. Beer's law holds within the limits of measurement for the solid solution series between $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NH}_4)_2 \cdot (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

2. Light absorption is at a maximum for wavelengths in the 6500 Å unit region and at a minimum for wavelengths in the region of 4900 Å for the α' and γ' vibration directions for crystals of $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ lying on a (110) face.

3. For the solid solution series studied light absorption measurements at several wavelengths generally permit prediction of composition to within 3 mol per cent.

4. The method can be used even though none of the pure end members of the solid solution series are available (since ϵ values may be computed for these end members from absorbance measurements on crystals of known but intermediate compositions).

5. Difference in absorbance per centimeter measurements for the wavelengths of maximum and minimum absorption of a crystal may be substituted into the equation for Beer's law to obviate the effects of flaws, cleavages, or opacities in the crystals. Random errors may be increased, however, by this method of calculation.

6. The method can well be used to determine concentrations of colorants for small idiochromatic crystals of the geologically important solid solution series.

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