

Optical absorption spectroscopy of doped materials: the $P2_13-P2_12_12_1$ phase transition in $K_2(Cd_{0.98}Co_{0.02})_2(SO_4)_3$

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Abstract

The use of optical absorption spectroscopy for the study of the changes in local distortions during phase transformations is discussed, with particular reference to the $P2_13-P2_12_12_1$ transition in $K_2Co_2(SO_4)_3$ langbeinite. In order to extend this technique to the study of cobalt-doped cadmium langbeinite, $K_2Cd_2(SO_4)_3$, the consequences of the doping with regard to site occupancies and low signal strength are discussed, and some details of data modelling are considered. The problem of modelling the spectrum of Finero sapphire is taken as an example, and it is shown that even simple and evidently inadequate models can provide useful information.

The results of optical spectroscopic investigation of the $P2_13-P2_12_12_1$ transition in $K_2(Cd_{0.98}Co_{0.02})_2(SO_4)_3$ langbeinite are presented. The trigonal splitting of the spin allowed ${}^4T_{1g}(F)-{}^4T_{1g}(P)$ transition has been determined, and shows a linear increase with increasing temperature in the high temperature cubic phase, and a constant value in the low temperature phase. This is in good agreement with previous structural work on this material, and it is concluded that optical spectroscopy of doped materials can provide useful information about site distortions.

KEYWORDS: optical absorption spectroscopy, phase transition, langbeinite, cadmium.

Introduction

OPTICAL absorption spectroscopy is a technique which has been applied to mineralogy for some years (Burns, 1970), but which, until recently, has been restricted mainly to determination of oxidation state, crystal field stabilization energy (CFSE) (including the influence of CFSE on phase transitions, for example Burns, 1978), and in some cases site occupancies. For details of previous mineralogical applications of optical spectroscopy see Langer (1988), Rossman (1988)

and references therein. Optical spectroscopy can also be used to measure local site distortions *in situ* during phase transitions, via the additional line-splitting that is produced by the distortion, which is measured from optical spectra obtained at temperatures above and below the transition temperature, as has been carried out in the case of a cobalt langbeinite, $K_2Co_2(SO_4)_3$, by Percival and Salje (1989). Unfortunately, many minerals do not contain any transition metals (or, if any, iron, from whose spectrum it is difficult to extract detailed site-distortion parameters, owing to variable oxidation state, the absence of spin-allowed bands in Fe^{3+} , and the extremely high line width

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(and therefore poor resolution) of the single spin allowed transition which is observed in Fe^{2+} , so samples doped with other transition metals have to be used in order to obtain satisfactory results. This raises technical problems owing to the small concentration of the target ion, and the possibility that the dopant does not lie on the site of interest, or does not correctly reflect the behaviour of that site.

It is the purpose of this paper to discuss the use of optical spectroscopy of doped samples for the observation of local distortion parameters during phase transitions, with particular reference to the study of the $P2_13-P2_12_12_1$ in cobalt-doped $\text{K}_2\text{Cd}_2(\text{SO}_4)_3$ langbeinite, and it will be shown that useful information can be obtained by this technique.

Theoretical background

The crystal field theory was first described by Bethe (1929), and is well described in many inorganic chemistry texts (e.g. Cotton *et al.*, 1987), and in greater detail in texts dedicated to the subject, for example Jorgensen (1962). Here I will merely mention briefly a few points which are relevant to the use of optical spectroscopy for the study of phase transitions.

In an isolated free ion of a transition metal, the five $3d$ orbitals are degenerate, and this degeneracy is preserved in a hypothetical 'spherical' field. However if the ion is placed in a crystal field of lower symmetry, for example an octahedral field, some of the orbitals are repelled more than others, and so the degeneracy is lifted. This effect is illustrated in Fig. 1, where it can be seen that in an octahedral field the five degenerate orbitals are resolved into two of higher energy (e_g) and three of lower energy (t_{2g}), separated by an energy difference Δ_o . This splitting of the energy levels gives rise to the possibility of absorption of electromagnetic radiation in the optical region of the spectrum, corresponding to the transition of an electron from the t_{2g} energy levels to the higher energy e_g levels. The value of the energy difference Δ_o depends on the magnitude of the crystal field, that is the strength of the repulsive effect of the surrounding ligands. This in turn is determined by two factors; the charge on the surrounding ligands (O^{2-} produces a stronger crystal field than Cl^- , for example), and the size of the site (closer ligands have a stronger effect than more distant ligands). Changes in the value of Δ_o produce changes in the energy at which absorption takes place, and thus it is possible to plot the absorption energy (or wavenumber) against the strength of the crystal field. These calculations

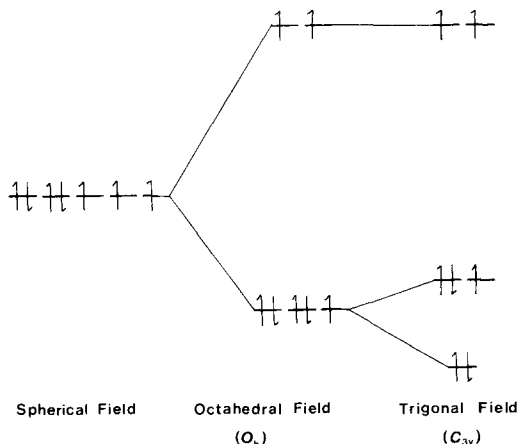


FIG. 1. Splitting of $3d$ energy levels in crystal fields of various symmetries. Occupation shown for a d^7 ion, e.g. Co^{2+} . (a) Spherical field. (b) Octahedral field, O_h . (c) Trigonal distorted octahedral field, C_{3v} .

were first performed by Tanabe and Sugano (1954*a, b*), and the resulting energy level diagrams are often referred to as 'Tanabe-Sugano diagrams', Fig. 2.

In a distorted site, the crystal field is similar to that in a perfect octahedron, so the general form of the optical spectrum will be the same. However, the symmetry of the crystal field is reduced from the O_h symmetry of a perfect octahedron, so the influence of the field on orbitals which are degenerate in an octahedral field is different. Thus the degeneracy of the orbitals is further lifted, with the exact details depending on the symmetry of the distortion. This is illustrated in Fig. 1 for the case of a trigonally distorted octahedron, with symmetry C_{3v} , where it can be seen that the t_{2g} orbitals are split into e_g and a_{1g} orbitals. This splitting gives rise to splitting of the observed absorption bands, since electrons may be transferred from either of the lower energy orbitals to the higher energy orbitals. These two transitions may have differing symmetry selection rules, and if this is the case they will be observed in light of differing polarizations. However, the 'splitting' can still be observed as the difference between the energy of the absorption maxima in the different polarizations. Throughout this work, unpolarized light has been used, so peaks corresponding to the different polarizations will be superimposed, and must be resolved via computer modelling techniques. This allows the resolution of peaks corresponding to transitions to different excited states, provided the energies of these transitions are sufficiently different, but does not pro-

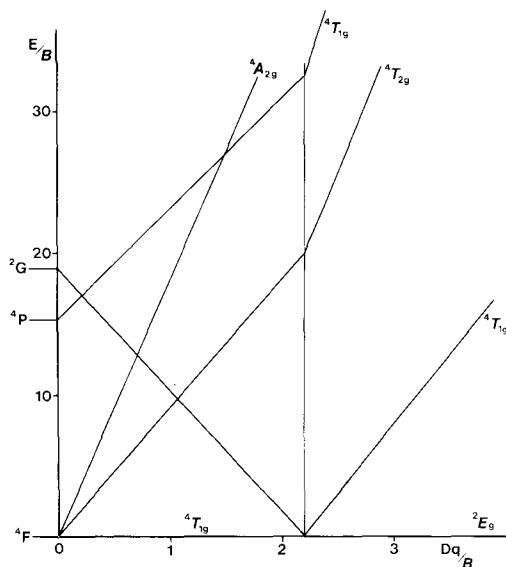


Fig. 2. Simplified Tanabe-Sugano diagram for d^7 ions. After Tanabe and Sugano (1954b).

vide any information concerning the differing intensity of a given transition in light of different polarizations, since these will be superimposed in unpolarized light. Thus the use of unpolarized light and computer modelling is suited to the study of line splitting and the distortion of sites, but not to the study of the polarization behaviour of the optical spectrum. The magnitude of the separation of the orbitals depends on the magnitude of the distortion, and thus the splitting of the observed optical absorption lines can be used as a measure of the magnitude of distortion of the site.

During a phase transition, cation sites frequently change symmetry, and the magnitude of the distortion of sites may be significant in controlling the phase transition. Thus by measuring the distortion of a site at various temperatures above and below the transition temperature (T_c) the behaviour of the site through the transition can be observed. Other techniques are, of course, available which can give the same information. However experimentally optical absorption spectroscopy is much simpler than many other techniques, since many optically transparent materials are available for the confinement of samples and the construction of furnaces. Thus it is relatively easy to take spectra at high temperatures and pressures (e.g. using a diamond anvil cell), and using a spectrometer attached to a microscope

spectra can be obtained from a small area of a sample.

The use of optical spectroscopy to follow a phase transition is illustrated by the example of cobalt langbeinite, $K_2Co_2(SO_4)_3$, studied by Percival and Salje (1989). They observed a splitting of the transition to the ${}^4T_{1g}(P)$ excited state, corresponding to a trigonal distortion of the CoO_6 octahedron. This distortion shows a linear temperature dependence in the high temperature (cubic) phase, increasing with increasing temperature, while below the transition temperature an 'excess distortion' above that extrapolated from the high temperature phase is observed. This is also a linear function of temperature, and falls continuously to zero at the transition temperature, consistent with a locally second order phase transition. This is inconsistent with the first order nature of the phase transformation in other langbeinites, predicted by Dvorak (1972), and observed experimentally by a variety of techniques (e.g. Lissalde *et al.*, 1979; Hikita *et al.*, 1978). However, it has been found (Devarajan and Salje, 1984) that the third order term in the Landau expansion, although symmetry allowed, has negligibly small value, and so the observation of an apparently second order transition is not impossible. Percival and Salje's observations, in conjunction with structural data (Percival *et al.*, 1989) have led to the identification of a trigger mechanism for the phase transformation in langbeinites.

As noted above, the use of a doped sample gives rise to additional problems of its own:

1. Does the dopant occupy the same site in the mineral as the cation it replaces?
2. Does the behaviour of the dopant correctly reflect the behaviour of the ion it replaces?
3. At what level of concentration is it possible to detect and analyse the absorption bands?

These three questions will be dealt with in turn.

The site occupied by the dopant atom will be controlled by the chemistry of the dopant and the availability of other sites in the structure. Thus it is important to select a dopant ion which is chemically as similar as possible to the ion being replaced, since this will have the greatest likelihood of occupying the same site. However the choice of dopant is also controlled by which of the transition elements give strong absorption features, and which will split in a manner which makes analysis of the site distortions easiest. Thus, for example, to probe the calcium site in anorthite, the choice on purely chemical grounds would be manganese. However manganese does not show any strong absorption features, so

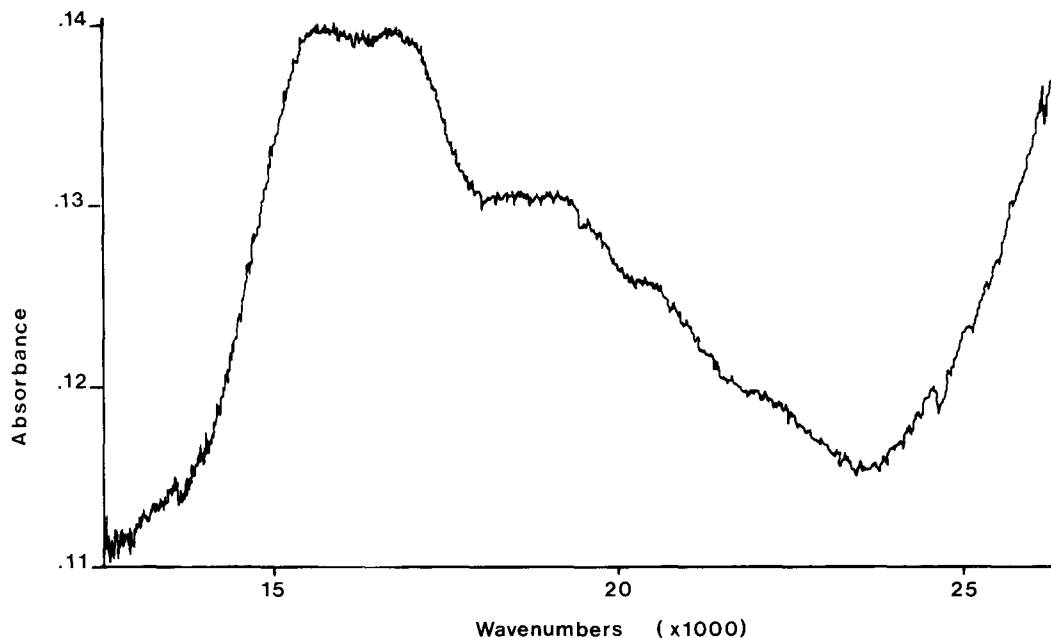


Fig. 3. Diffuse reflectance spectrum of cobalt doped anorthite, $\text{Ca}_{0.98}\text{Co}_{0.02}\text{Al}_2\text{Si}_2\text{O}_8$. Sample prepared as a gel of appropriate composition by the method of Hamilton and Henderson (1968), recrystallized at 1770K and 1 atmosphere in air for 46 hours. Spectrum obtained using an MgO coated integrating sphere, and MgO as the white standard.

another, chemically less suitable transition metal must be used instead. The element which gives the best results from a spectroscopic point of view is cobalt, since this has a single, very intense, spin allowed absorption band at around 19000cm^{-1} , and no other significant features in the optical part of the spectrum.

From the optical spectrum, it is often possible to ascertain whether the dopant occupies the desired site in the structure, provided good structural data are available. As noted above, the positions of absorption lines in the spectrum depend on the strength of the crystal field, which is in turn determined by the size of the site. Thus the observed position of the line can be used to estimate the size of the site occupied by the dopant. This is illustrated in the case of a cobalt doped anorthite (Fig. 3), where the main absorption feature is observed at between 15000cm^{-1} and 17500cm^{-1} . These frequencies are much lower than is normal for cobalt surrounded by oxygen ligands, for example Percival and Salje (1989) observe the same transition in $\text{K}_2\text{Co}_2(\text{SO}_4)_3$ at around 18700cm^{-1} . This suggests that the cobalt in anorthite occupies a much larger site than usual, since a larger site implies a smaller crystal field and therefore a lower energy for the absorp-

tion line, which is consistent with the cobalt lying on one or more of the calcium sites, which have bond lengths in the range $2.32\text{--}2.72\text{Å}$, compared with around 2.08Å for $\text{K}_2\text{Co}_2(\text{SO}_4)_3$. If the cobalt were occupying an interstitial site, or if it had formed a second compound in concentrations too low to be detected by X-ray powder diffraction, then it would be expected that the site would be closer in size to those normally occupied by cobalt.

In some cases, however, it is not possible to determine directly from the spectrum whether the dopant is occupying the correct site in the structure. In these cases, some other technique must be used, and in this context element specific techniques such as EXAFS may prove particularly suited, since comparison can be made directly between the environments of the dopant and the atom which it replaces.

The second question posed above is whether the dopant behaves in the same way as the atom it replaces. Provided the concentration of the dopant is small, the presence of these impurities will not produce distortions in the crystal structure as a whole, especially in cases where the crystal structure is strongly defined by a feature in which the substituted cation plays no part, for example

the Al/Si framework in anorthite or the SO_4 tetrahedra in langbeinite. Under these conditions, as noted by McClure (1962), a dopant ion at a substitutional site will be subject to a crystal field which is approximately the same as that of the undistorted crystal. McClure considers the example of ions substituting for aluminium on a trigonally distorted octahedral site in corundum. The Al ions lie on the threefold axis, but are displaced from the centre of the octahedron through a distance w . The value of this displacement is not expected to be the same for an ion substituting for Al, but the symmetry of the force system of the crystal acting on the foreign ion is the same as that acting on the Al, so the substituting ion is not permitted to depart from the threefold axis. Thus the substituting ion will lie on a site of the same symmetry, but may be displaced through a different distance. Since the force systems acting on the Al and the substituting ion are the same, it is expected that the displacement of the substituting ion (w_{sub}) will be linearly related to that of the aluminium (w_{Al}): $w_{\text{sub}} \propto w_{\text{Al}}$. Thus it is expected that a substituting ion will in fact give a true measure of the distortion of the site it occupies, even if the calibration of the line splitting as a measure of the actual distortion of the site may not be straightforward.

The final question concerns the concentration of dopant necessary to obtain a signal which is sufficiently strong to be measured and analysed. This question is a logical follow-up to the previous one, since if the concentration required is large, then it will be sufficient to produce distortions of the lattice, which will destroy the arguments used in the previous paragraph. There is no simple minimum concentration required; the signal strength depends on the dopant ion used, and on the site occupied, while the noise level depends on the temperature required. Finally, the signal to noise ratio required to extract the maximum information depends on the complexity of the peak; a simple peak split into two components (as in the langbeinites) is relatively easily modelled, while the anorthite peak is made complicated by the fact that there are four different sites, each of which gives rise to a peak split into two major components, requiring much more complicated modelling. In order to extract useful information from such a spectrum, a much higher quality spectrum is required.

Of all the transition metals, the spin allowed transition from the ${}^4T_{1g}(F)$ groundstate to the ${}^4T_{1g}(P)$ excited state in Co^{2+} has the greatest intensity, and in addition this line shows easily measurable splitting. Thus cobalt is an ideal dopant, and it is found that 2% cobalt provides

an easily measurable signal (about 0.07 absorbance units) in cadmium langbeinite ($\text{K}_2\text{Cd}_2(\text{SO}_4)_3$), and a rather lower but useable signal (around 0.03 absorbance units) in anorthite. In both of these materials the lattice parameters show no evidence of distortion of the host structure.

The final answer to the question of the concentration required, however, depends on the sophistication of the data modelling attempted.

Data modelling

The extraction of information from optical spectra depends on computer band stimulation. This process can be divided into two stages: (1) Background fitting; (2) Peak fitting.

Background fitting. Three different shaped backgrounds can be used, depending on the sample under investigation:

In the case of a very strong absorption feature, such as that observed by Percival and Salje (1989) in $\text{K}_2\text{Co}_2(\text{SO}_4)_3$, a simpler linear background joining points on either side of the absorption line can be used. In these cases, the distortion of the peak produced by the use of a linear background is small relative to size of the peak.

In the case of samples containing a low concentration of the absorbing species, however, a non-linear background needs to be used to reflect the variation in background absorption with wavenumber, so as not to distort the shape of the peak under investigation. The shape of this background depends on the phenomenon leading to absorption; in the case of a background increasing at higher wavenumber due to dispersion from imperfections in the crystal, then an exponential background is appropriate, while if the background is due to charge transfer absorption, or to other underlying broad absorption features, then a gaussian background may be used. Under some circumstances a combination of two or more background curves may be used, and care must be taken in identifying points which lie on the background, which are used in modelling it.

Peak shape. The most commonly used peak shape is the gaussian error curve, although several authors (e.g. Wood, 1965; Parkin and Burns, 1980; Percival and Salje, 1989) note that the observed absorption lines are, in fact, somewhat skew. Parkin and Burns suggest that extra parameters may be needed to describe this distortion, but this has not been attempted in practice. Grum-Grzhimailo and Klimusheva (1960) found that the deviation from a gaussian peak shape is greatest at low temperatures, while at higher temperatures, where $2B/T \gg 1$ (B is a parameter related

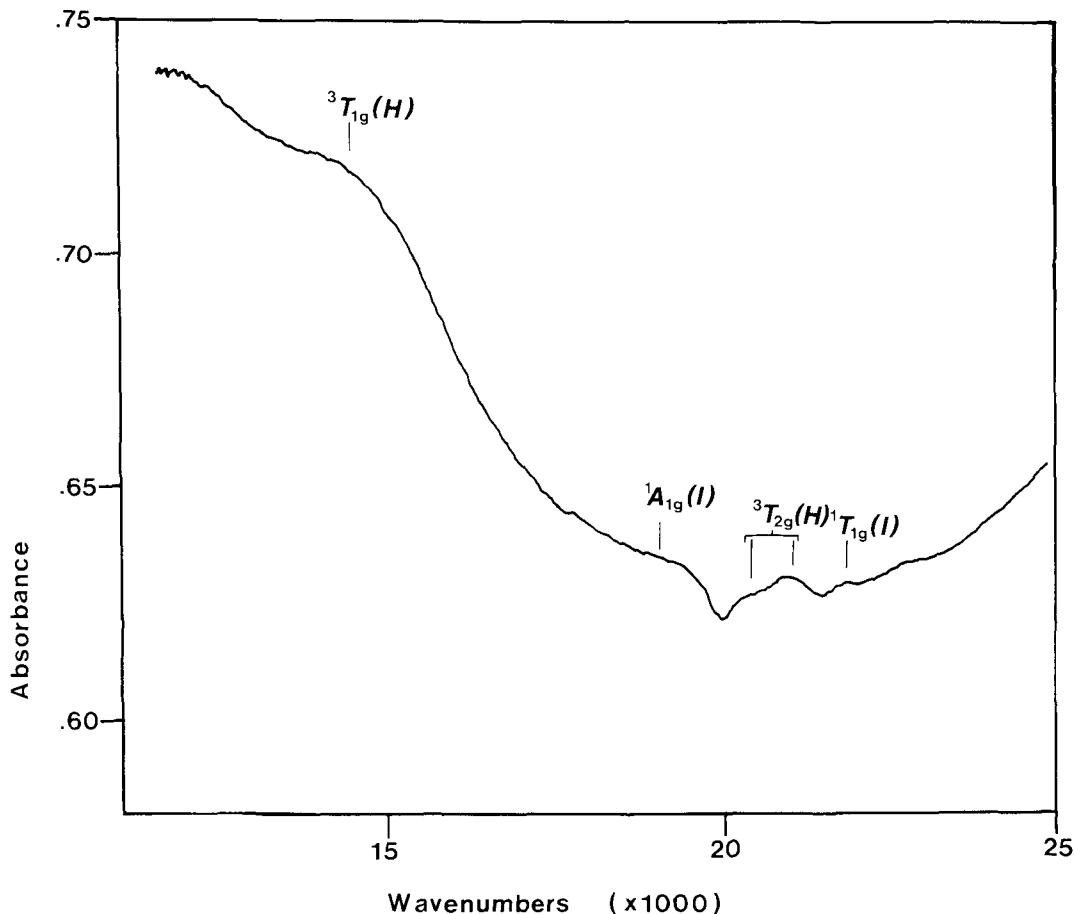


Fig. 4. Unpolarized transmission spectrum of Finero sapphire, after Percival and Christy (in preparation). The ground state for all transitions is ${}^5T_{2g}(D)$.

to the half width of the absorption band, and T is the reciprocal of the lifetime of an impurity centre in the excited state) the absorption band does have a gaussian shape. Thus for most mineralogical applications, where the interest is in phase transformations above room temperature, the use of a simple gaussian peak shape is perfectly adequate. The model used for peak fitting, then, is a number of gaussian curves, one for each split component of the transition from each site occupied by the transition metal.

An additional assistance in the fitting of the split components comes from the fact that the split parts of a single transition are expected to have the same linewidth (Vainshtein and Antipova-Karataeva, 1959). Thus the model can be constrained by forcing the split components of a single transition from a single site to have the same

linewidth, and this method has been found to give good results in langbeinite (Percival and Salje, 1989) and sapphire (Percival and Christy, in preparation).

Modelling sapphire: an example. The process of data modelling in optical spectroscopy is illustrated for the case of sapphire, which was studied by Percival and Christy (in preparation) to investigate the ordering of Fe^{2+} on the various sites in the structure. The spectrum of a sample of Finero sapphire containing 0.3 Fe^{2+} per formula unit is shown in Fig. 4, together with the peak assignments of Percival and Christy. The spectrum is dominated by broad absorption features at the extreme ends, with a number of weak spin forbidden bands superimposed on this outline. Percival and Christy used the ${}^3T_{2g}(H)$ peak to analyse the site distribution of the Fe^{2+} ; clearly

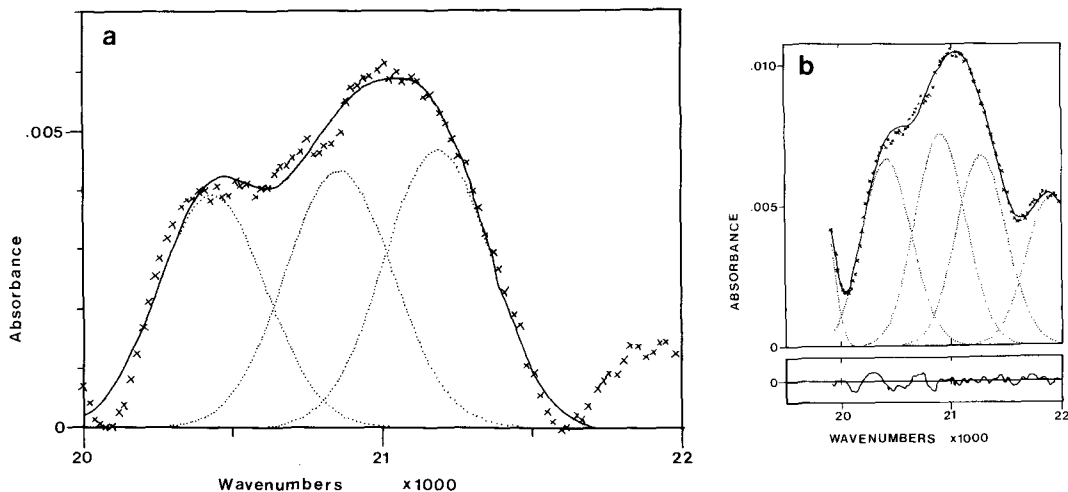


FIG. 5. Computer fits of the ${}^5T_g(D)$ - ${}^3T_g(H)$ peak of Finero sapphirine. x = data points, solid lines represent model (and, in (b), residual), dashed lines represent components of the model. (a) linear background. (b) curved background.

the background in this region is highly non-linear, being composed of components from the two main absorption features, with additional components from the neighbouring ${}^1A_{1g}(I)$ and ${}^1T_{1g}(I)$ peaks. There is also some doubt as to whether the lowest point in the spectrum (between the ${}^1A_{1g}(I)$ and ${}^3T_{2g}(H)$ peaks) lies on the background. The octahedral sites in sapphirine all have triclinic symmetry, so it would be expected that the ${}^3T_{2g}(H)$ peak would be split into three components for each site occupied by Fe^{2+} .

The first attempt to model this spectrum was made using a straight background, connecting points on either side of the peak. This is clearly an unrealistic background, since it does not reflect the overall shape of the spectrum, and does in fact intersect the spectrum at higher frequencies, and the assumption is made that the lowest point referred to above does indeed lie on the background. Superimposed on this background are three gaussians of the same linewidth, representing the three components of the ${}^3T_{2g}(H)$ peak from Fe^{2+} at a single site. Despite the simplicity of this model, a remarkably good fit is achieved (Fig. 5a), but it is apparent that the points used to fit the background do not in fact lie on the background.

The general shape of the spectrum, and the form of the absorption bands at each extreme end of the spectrum, led to the use of a background composed of a pair of gaussians, fitted to points at the extreme ends, and passing below the low point in the centre of the spectrum (Fig. 6). Using

this background, the model used must include contributions from the neighbouring peaks, so a system of three gaussians of the same width, plus two other gaussians, has been used (Fig. 5b). In this case a very good fit is achieved, and Percival and Christy concluded that there was no evidence for the presence of Fe^{2+} in more than one site in the crystal structure.

The change from linear to curved backgrounds produces a change in the parameters of the peaks; the lowest wavenumber component is shifted to lower wavenumber by 5.7cm^{-1} , the central component to higher wavenumber by 54.6cm^{-1} , and the high wavenumber component to higher wavenumber by 91.4cm^{-1} . However the ratio of the separation of the first two components to the separation of the second two remains almost constant (1.30 for a linear background, compared with 1.33 for the curved background). This effect illustrates a fact which is very important in the use of optical spectroscopy for the study of phase transitions, that changes in the model may produce changes in the absolute values of the parameters, but that the relative changes are more or less independent of the model used. This effect is even more marked when comparisons are made between spectra of one material obtained at different temperatures; the absolute values of line positions will depend on the background and model used, but the changes from one temperature to another will be correctly measured, provided the same model is used at all temperatures, and that a good fit is obtained using this model.

Co-doped cadmium langbeinite, $K_2Cd_2(SO_4)_3$

To explore the application of optical spectroscopy of a doped sample to the study of phase transitions, spectra have been obtained from a sample of Co-doped $K_2Cd_2(SO_4)_3$ langbeinite containing about 2% Co replacing Cd. The crystals were grown by the Bridgman technique, and

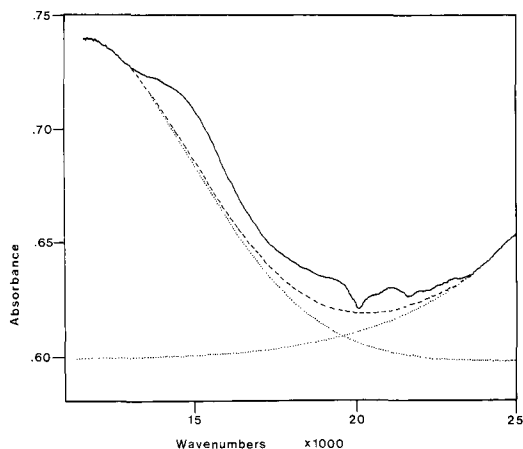


Fig. 6. Curved background used in modelling Finero sapphirine. Solid line = data, dashed line = model background, dotted lines represent components of background.

were supplied by Dr U. Bismayer (Hannover). Structural studies have been carried out by Percival *et al.* (1989). The sample shows a first order transition from a high-temperature cubic space group, $P2_13$, to a low-temperature orthorhombic phase, $P2_12_12_1$, with a critical temperature of 430.5 K.

Experimental. One face of a crystal of approximately $2 \times 2 \times 1$ mm was polished, and this was then glued to a disc of copper having a hole 1 mm in diameter in the centre. The opposite face was then polished giving a sample approximately 0.5 mm in thickness, which was placed in a furnace capable of heating it in excess of 1000 K, the whole arrangement being placed in the sample chamber of a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer. Unpolarized transmission spectra were measured from 4000 – 40000 cm^{-1} at a variety of temperatures, but at the highest temperatures measured (above 550 K) the noise level produced by radiative interference from the furnace was so high that the infrared part of the spectrum (below 11600 cm^{-1}) was not measured. Unpolarized light was used, and no attempt was made to orient the sample, since the main interest of the work was

focused on the behaviour of the high-temperature, cubic, isotropic phase. The only peak observed is at around 18000 cm^{-1} , corresponding to the ${}^4T_{1g}(P)$ peak in pure cobalt langbeinite (Percival and Salje, 1989); this peak is illustrated in Fig. 7.

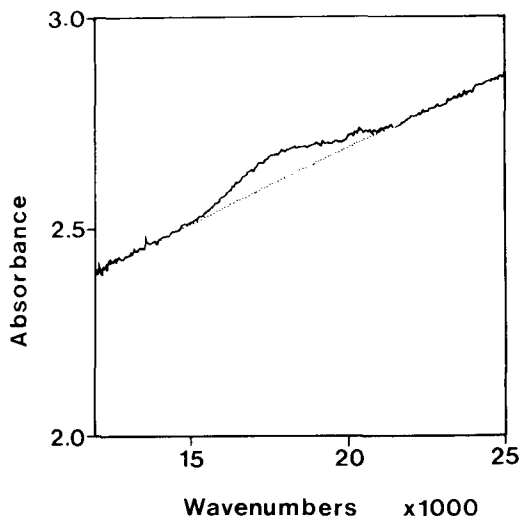


Fig. 7. Unpolarized transmission spectrum of $K_2(Cd_{0.98}Co_{0.02})_2(SO_4)_3$ at 487 K. Dotted line represents the background used in subsequent fitting.

Data modelling. The background is observed to curve slightly, flattening out at higher frequencies, so a gaussian background was used, as illustrated in Fig. 7. Following the subtraction of the background, the peak can be seen (Fig. 8) to be composed of a main peak, with a slight asymmetry owing to the splitting of the ${}^4T_{1g}(P)$ absorption line, with a narrower additional peak on the high wavenumber side. This extra peak is due to one of the spin-forbidden transitions in Co^{2+} , and will not be assigned to a particular transition, but it must be included in the model used to fit the peak. The peak is of identical shape to that observed by Percival and Salje (1989) in pure cobalt langbeinite, $K_2Co_2(SO_4)_3$, in which the cobalt site has identical symmetry to that in $K_2Cd_2(SO_4)_3$. As discussed there, the ${}^4T_{1g}(P)$ peak observed in unpolarized light is expected to be composed of two components in the high temperature phase, corresponding to transitions of electrons to two different excited states which would be degenerate in symmetry O_h , but are resolved in the lower symmetry (C_3) of the M^{2+} site in langbeinites. Thus the model used at high temperatures consists

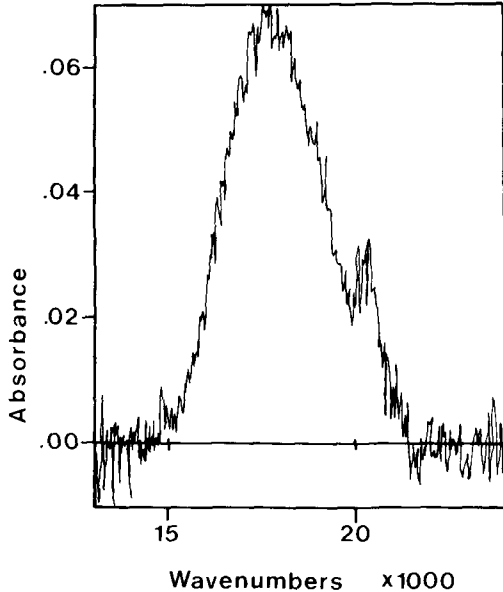


Fig. 8. ${}^4T_{1g}(F) - {}^4T_{1g}(P)$ peak in $K_2(Cd_{0.98}Co_{0.02})_2(SO_4)_3$ at 487 K following subtraction of background.

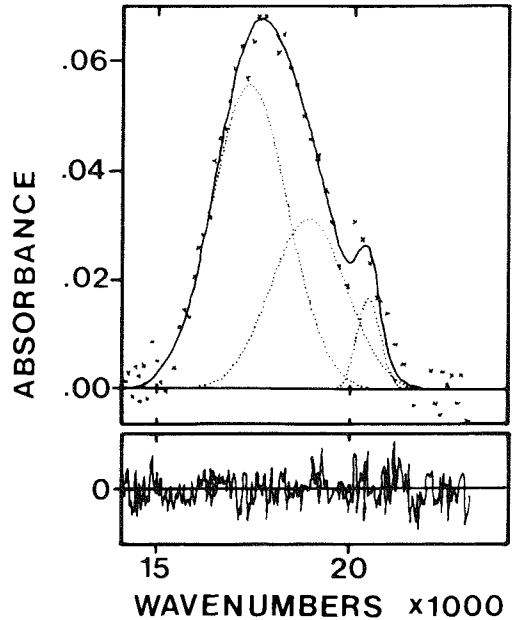


Fig. 9. Fitted ${}^4T_{1g}(F) - {}^4T_{1g}(P)$ peak in $K_2(Cd_{0.98}Co_{0.02})_2(SO_4)_3$ at 487 K: x = data points, solid lines represent model and residual, dashed lines components of fit.

of two gaussians of the same linewidth for the main peak, plus an additional gaussian for the spin forbidden band. At temperatures below T_c the site symmetry is reduced, and therefore further splitting of the peak is to be expected. However the distortion from symmetry C_3 is small, so the additional splitting will be small. Percival and Salje found in $K_2Co_2(SO_4)_3$ that the additional splitting cannot be resolved, but that the symmetry can be approximated as C_3 , and the same model can be used as above T_c . In $K_2Co_2(SO_4)_3$ the additional splitting is manifested as an excess linewidth below T_c . Thus in the current work the same model was used above and below T_c . The validity of this model is confirmed by the correlation of the results of optical spectroscopy with the distortion as measured by X-ray structure refinement, where an approximation to C_3 symmetry was made, as discussed below. The fitting was carried out using the same non-linear least squares fitting programme described by Percival and Salje, and an example of the fitted spectrum is illustrated in Fig. 9.

Discussion. Owing to the low signal strength of the spectra, which is a consequence of the low concentration of cobalt in the structure, a rather high noise level is observed, particularly in those spectra obtained at higher temperatures, where

interference from the furnace is more significant, and there is a rather large error in the parameters which describe the components, making it difficult to draw conclusions from the parameters themselves. However, as noted above, the line splitting parameter, used to measure the trigonal distortion of the cobalt site, is expected to be correctly measured even under these conditions. The temperature dependence of the splitting of the ${}^4T_{1g}(P)$ peak is plotted in Fig. 10a, and is seen to show a marked temperature dependence in the cubic phase. At T_c , an abrupt increase is observed, and then in the low-temperature phase a constant value of the line splitting is observed. The error bar shown is an estimate of the uncertainty of the magnitude of the splitting, and may be a considerable overestimate.

The trigonal distortion measured by this technique can be compared with that measured by structural means by Percival *et al.* (1989). They defined a 'Bond Length Variation Parameter', which measures the difference between the long and short bonds in the trigonally distorted octahedra. The temperature dependence of this parameter for the M2 site is illustrated in Fig. 10b, and that for the M1 site shows exactly the same temperature dependence. The BLVP is expected

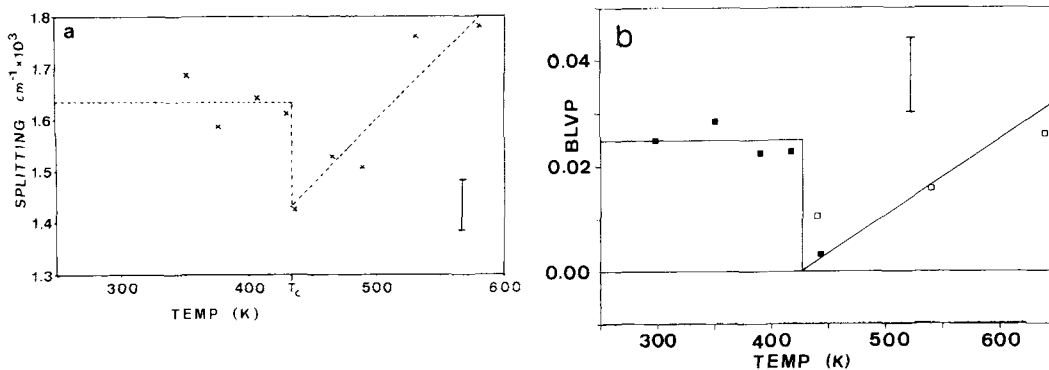


Fig. 10. Temperature dependence of distortion parameters of octahedral sites in $K_2(Cd_{0.98}Co_{0.02})(SO_4)_3$: (a) Splitting of $4T_{1g}(F) - 4T_{1g}(P)$ peak. (b) BLVP of M2 site (after Percival *et al.*, 1989).

to be correlated to the line splitting since they are both measures of the trigonal distortion of the octahedral site, and this correlation can be clearly seen in Fig. 10. The temperature dependence of the two parameters is identical, and thus it is possible to conclude that the optical spectra do provide a good measure of the trigonal distortion. In passing we notice that each data point in Fig. 10a represents about 3 hours data collection and analysis, while each data point in Fig. 10b represents about 8 weeks data collection and analysis.

Conclusions

The most important conclusion to be drawn is that useful information can indeed be obtained from optical spectroscopy, as illustrated by the example of Co-doped cadmium langbeinite. Provided that the dopant occupies the correct site in the structure, this technique can be used to measure the changes in site distortion through a phase transition.

Where the interest is in relative changes (e.g. from one temperature to the next in the case of a phase transition), slight inadequacies in the model are not, in general, significant, since relative changes will be correctly reflected even if the absolute values of the parameters are wrong.

The final conclusion is that optical spectroscopy, like other techniques in mineralogy, should not be used in isolation. Complementary techniques, such as X-ray structure determination and EXAFS, should be used to check the site occupancy of the dopant, and to aid in the interpretation of the spectra.

Acknowledgements

Thanks to Mr B. Cullum for the construction of the furnace used in this research, and to Dr C. Pereira for the use of the spectrophotometer. This work was supported by the United Kingdom NERC, grant number GT4/86/GS/18. This paper was presented at an open meeting of the Mineralogical Society held at Burlington House, Piccadilly, London, on April 20th 1989.

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- [Manuscript received 27 April 1989; revised 12 March 1990]