

INFRARED ABSORPTION EFFECTS, NUCLEAR MAGNETIC RESONANCE AND STRUCTURE OF FELDSPARS

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Abstract

Infra-red absorption spectra and nuclear magnetic resonance measurements of several alkalifeldspars (sanidine, adularia, microcline, albite and heattreated albite) are presented, and the problems of the Al/Si-distribution within these feldspars are discussed. The most direct conclusion could be drawn from the NMR-measurements; they proved that in microcline(low) and albite(low) Al occupies only one of the four available lattice complexes and that there is nearly random distribution in the high temperature states.

Introduction

Among the problems confronting the petrographer engaged in the study of feldspars, two are perhaps of particular importance.

1. It is well known that the Al/Si distribution often plays a decisive role in the phase relations of feldspars. Several of the phase transformations are almost entirely dependent on the order/disorder of the Al/Si-distribution, the topology of the silicate framework remaining practically unchanged and the lattice constants and angles changing only slightly. Due to the low symmetry, more than two sets of equivalent points for Al and Si are frequently available. Therefore cases with partly ordered distributions between the completely ordered and disordered limiting cases become extremely numerous. Besides partially

ordered *stable* Al/Si distributions, an additional unlimited number of *unstable* ones can be visualized.

An experimental determination of the exact distribution of Al and Si in the possible lattice complexes of a feldspar would usually involve great and often perhaps insurmountable difficulties; the determination of even an approximate mean Al/Si distribution will in many cases be very hard to obtain without a great deal of work. It appears, for instance, that in the potash feldspars it may be dangerous in cases to make conclusions about the degree of order/disorder from the optical properties, from the symmetry of the lattice (for instance from the "triclinicity") or from the size of the lattice constants or lattice angles. Although the degree of splitting of the hkl and $h\bar{k}l$ reflections usually gives a rough estimate of a minimum degree of order, the splitting may also be influenced by other factors such as domain-size, Ab content etc.

2. Examination of different feldspars has shown that crystals which appear to be optically homogeneous may in reality be aggregates consisting of many very small triclinic domains of single-crystal character. Good examples of this are the finely twinned microclines. Orthoclase and K-feldspars of adularia type may behave similarly although they give sharp X-ray reflections which can be indexed on a monoclinic cell. Various X-ray observations (e.g. "Diffuse reflections" Laves, 1950) gave evidence for such an assumption.

Two other physical methods appear suitable for obtaining more direct information about the problems outlined above: (1) Infra-red absorption and (2) Nuclear magnetic resonance. Both methods are sensitive to order/disorder phenomena. They have further the advantage that the effects caused by the Al/Si distribution can be separated to a large extent from the effects caused by the lattice symmetry and the lattice dimensions. Therefore it should be possible—at least theoretically—to estimate the degree of order of the Al/Si-distribution independently of the chemical composition of the feldspar, i.e. independently of the Na, K or Ca content.

Both methods give information on the immediate surroundings of Si and Al (infra-red absorption) or of Al and Na (nuclear magnetic resonance). The spectra measured largely depend on the position of the surrounding ions within a small volume of approximately unit-cell size. Therefore these methods should give indications concerning

the Al/Si-distribution, even if the feldspars consist of very small domains.

Infra-red absorption spectra

Feldspars show several absorptions between 8 and 25 μ whose wavelengths and intensities depend on the structure and the chemical composition. The absorptions are caused by the fundamental, infra-red-active vibrations of the feldspar structure. It is probably correct to correlate the short-wave absorption bands (between 8.5 and about 15 μ) with the fundamental internal vibrations of the (Al,Si)O₂ framework, i.e. the internal vibrations of the SiO₄⁻ and AlO₄ tetrahedral groups. Therefore, these absorptions are due to Si-O or Al-O valency vibrations. Vibrations in which the SiO₄⁻ or AlO₄ tetrahedra behave more or less as rigid bodies should be expected to occur in the longer-wave portion of the spectrum. The same probably also applies to valency vibrations between the alkali or alkali-earth ions and oxygen. In addition, numerous, often relatively sharp absorptions can be observed in the 4 to 7 μ range. These absorptions are about 100 times weaker than those between 8 and 25 μ . They can be designated as *overtone* and *combination vibrations*.

1. Fundamental vibration

Powder spectra

Figures 1 and 2 show the absorption spectra of powders of some K- and Na-feldspars. The ordered Al/Si-distributions (albite and maximum microcline) correspond to sharp absorptions while the disordered distributions (sanidine, heated albite and heated microcline) give rise to a considerable broadening. A detailed description of the spectra of some plagioclases, of the unstable solid solution series albite-microcline, as well as a description of the absorptions of some alkali feldspars after various heat-treatment was given by Laves and Hafner (1956) and Hafner and Laves (1957). The experimental method is described in these papers.

Figure 3 is an example of the possible application of the infra-red method. It shows the spectra of three K-feldspars of adularia type. Spectra 3a and 3b are specifically characteristic of adularia (more than 50 adularias were examined). Hafner and Laves (1957) have

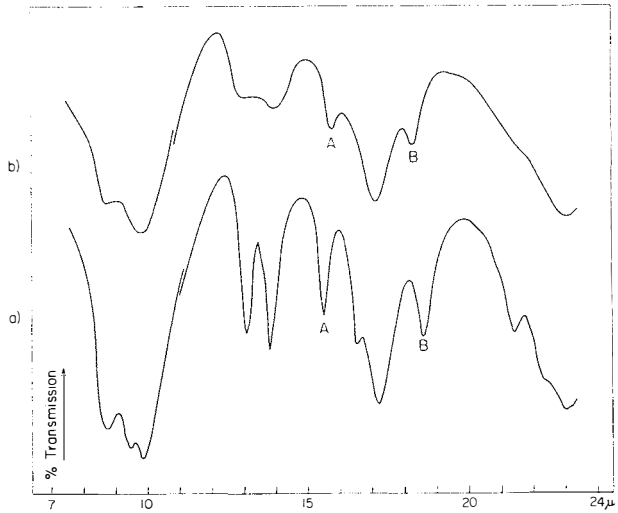


Figure 1. Infra-red absorption curves of maximum microcline, Crystal Peak, Col. (a), and of the same material heated at 1050°C, 30 days (b). Powder method, 0.8 mg. For the range 7–11 μ a NaCl prism was used, for the range 11–24 μ a KBr prism.

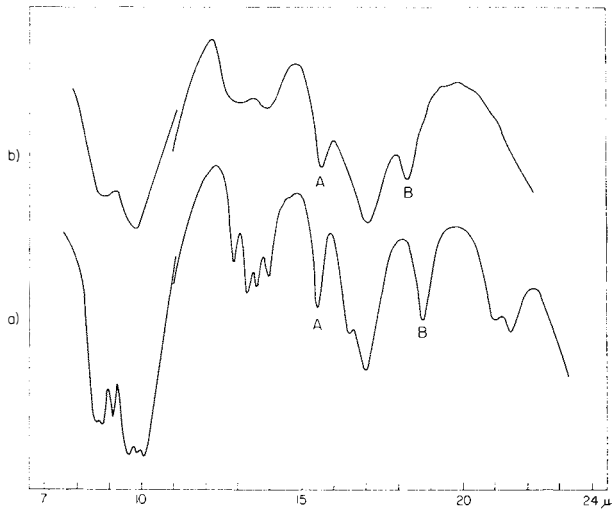


Figure 2. Infra-red absorption curves of albite (low), Amelia, Virg. (a), and of the same material heated at 1050°C, 28 days (b). For experimental information see Figure 1.

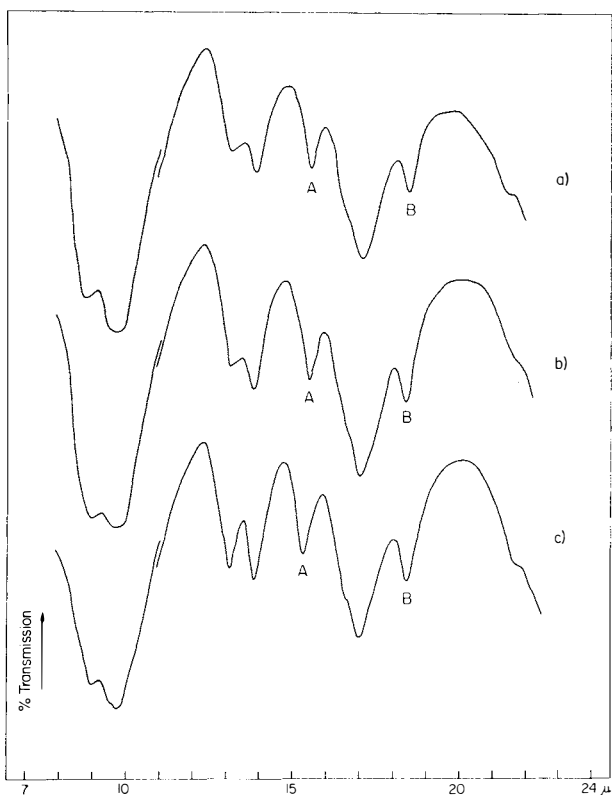


Figure 3. Infra-red absorption curves of adularia, optically monoclinic; (a) Disentis, Switzerland, (b) Piz Blas, Switzerland, material from the core, (c) Piz Blas, material from the rim. Note that curve *c* corresponds more to a microcline curve (figure 1a) than to a sanidine curve (figure 1b).

especially measured the two absorptions *A* and *B* in the long wavelength part of the spectrum (cf. Figure 3) and compared them with the corresponding bands of microcline and sanidine. It was found that the wavelengths of *A* and *B* of the adularias are scattered over the whole range between those of microcline and sanidine, and, indeed, often lie nearer to microcline than to sanidine (cf. Figure 2*b* in the paper just quoted). The adularia spectrum can be explained satisfactorily by the assumption (Laves, 1950), that adularia—although appearing monoclinic and optically homogeneous—often consists of aggregates of small, essentially ordered, twinned triclinic domains.

Regions must exist at the domain boundaries which have higher disorder or an altered structure (in the sense of Laves and Goldsmith, (1961), Figure 4) from which may be explained the relative width of the bands, especially in the short wave part of the spectrum.

The adularia spectrum of Figure 3c is a good example which supports the above interpretation of the adularia structure. Although this K-feldspar is optically monoclinic and has the typical adularia habit, its infrared spectrum is very similar to that of maximum microcline. The sample was taken from the rim; its core gives the usual absorption curve (Figure 3b). Apparently, in the rim the domains are so large and so ordered that the specimen behaves like maximum microcline in its infra-red absorption spectrum, whereas it even appears monoclinic when investigated with X-rays if the sharp reflections are considered only. A precession photograph of this rim material was presented (as Figure 8) by Laves and Goldsmith (1961)).

Single crystal spectra

The measurement of the absorption behaviour of oriented thin sections of single crystals in polarized light gives naturally more exact information than the spectra of powders. However, difficulties arise because sections 3–4 μ thin are required. The application of the reflection method should help. Investigations in this direction are in progress.

2. Overtone and combination vibration

The overtone and combination vibrations of the feldspars are so numerous that they overlap in powder spectra and are thus not easily studied. Oriented thin sections of single crystals (thickness about 0,1 mm.) and polarized light are required. As far as can be judged from the previous results carried out on some alkali feldspars, sharp absorptions are only obtained from feldspars with a well ordered Al/Si-distribution. The intensity of the bands is in general clearly dependent on the orientation of the crystal with respect to the plane of polarization of the light. With increasing disorder the bands become very broad. Their behaviour thus corresponds essentially to the absorption of the fundamental vibrations. Sanidine and albite heated for long periods of time at 1050°C have practically no well resolved

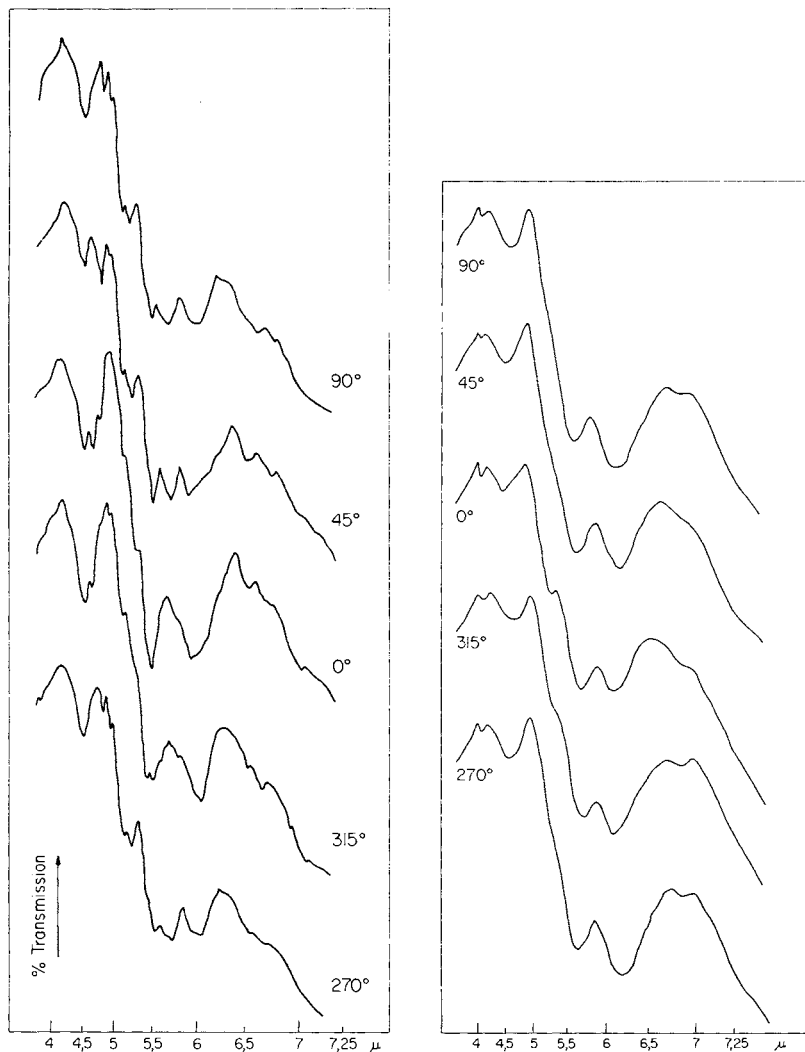


Figure 4. Single crystal infra-red absorption curves of microcline, Pellotsalo, Finland, (a), and sanidine, Wehr, Eifel (b). Sections 0.1 mm. thick, parallel to (010) were used; polarized light (CaF₂ prism). At 0° the electric vector of the incident beam was parallel to the *a*-axis. Note the strong "pleochroism" in (a) compared to (b). In the case (a) a microscopic attachment was used (double beam method) because only very small areas free from albite existed in the specimen.

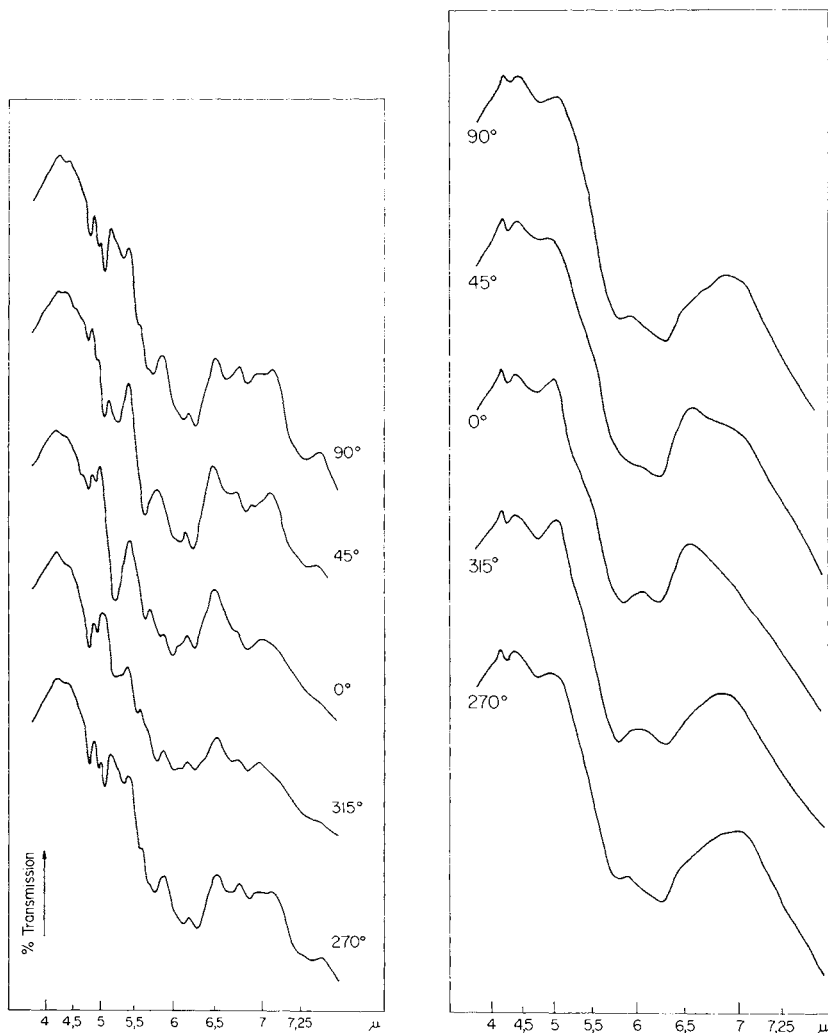


Figure 5. Single crystal infra-red absorption curves of albite (low), Amelia (*a*), and of the same material heated at 1050°C, 28 days (*b*). For experimental information see Figure 4.

bands any more. The strong orientation dependence of the spectrum has virtually vanished. Figures 4 and 5 show the absorptions of microcline, albite, sanidine and heated albite for various orientations of the crystals relative to the plane of polarization.

3. Concluding remarks on infra-red absorption spectra

The relations between the infra-red absorption spectra and the feldspar structure can be summarized as follows:

α) Feldspars with ordered Al/Si-distributions show sharper absorptions (with smaller half widths) than those with disordered distributions. Some absorptions also change their wavelength.

β) The influence of the lattice dimensions (in the microcline-albite series) expresses itself mainly in the displacement of the peaks. The half widths are changed very little or not at all. Certain bands become split. Compare for example the splitting of the two absorptions of microcline at 13.0 and 13.8 μ , Figure 1a, into the four absorptions of albite (12.75, 13.2, 13.5 and 13.85 μ , Figure 2a).

γ) The considerable broadening of the bands with increasing disorder can be best explained as follows: When an ordered distribution is present in the structure all translationally identical Si and Al ions have the same neighbourhood with exactly the same positions of the surrounding ions. When a disordered distribution is present the positions of the oxygen ions are slightly changed. Each Si and Al ion has differently distributed neighbours, as well as a slightly different geometry of its immediate neighbourhood. Thus practically an infinite number of oscillators exists, which are out of tune relative to each other (because of the variation of the force constants within certain limiting values).

Nuclear magnetic resonance spectra

Nuclear magnetic resonance allows the observation of the electric quadrupole splitting of the atomic nuclei in crystals. By electric quadrupole splitting is understood the splitting of the Zeeman resonance line of a nucleus in a magnetic field into two or more lines. The necessary conditions for the occurrence of quadrupole splitting are a nuclear spin quantum number I greater than $1/2$, a non-zero electric quadrupole moment of the nucleus, and a non-cubic point symmetry at the site of the nucleus. The electric crystal field gradient $\vec{\nabla E}$ at the site of the nucleus can be obtained from the measured splitting. $\vec{\nabla E}$ possesses the properties of a tensor:

$$\vec{\nabla E} = \begin{array}{ccc} + \frac{\partial E_x}{\partial x} & 0 & 0 \\ 0 & + \frac{\partial E_y}{\partial y} & 0 \\ 0 & 0 & + \frac{\partial E_z}{\partial z} \end{array} \quad \begin{array}{l} \vec{E} \text{ electric crystal field} \\ \\ \\ x, y, z \text{ system of coordinates} \\ \text{fixed to the lattice} \end{array}$$

$$\frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} = 0$$

If all atoms A (with nuclear spin quantum number I) of a crystal occupy one single lattice complex [1] consisting only of translationally identical points, the nuclear magnetic resonance spectrum possesses $2 \cdot I$ signals. The positions [2] of the signals depend on the orientation of the crystal with respect to the magnetic field \vec{H}_0 . They are determined by the angles between $\vec{\nabla E}$ and \vec{H}_0 . The number of the signals increases, when, in addition, other equivalent points are present in the lattice complex (e.g. points related by reflection) or when A occupies two or more lattice complexes in the crystal. In the last case different field gradients occur at the different sites of the A nuclei.

The magnitude and the orientation of the field gradient $\vec{\nabla E}$ depend sensitively on the symmetry of the lattice, on the atomic coordinates, as well as on the electric charges and the electronic configurations of the surrounding ions in the structure. An examination of the number of signals and the experimental determination of the one or several field gradients—if one or several lattice complexes are present—gives valuable information for a deeper understanding of crystal structures.

Of the common atoms in feldspars, only Al^{27} and Na^{23} are at present suitable for the study of quadrupole splitting effects, since they only have a nuclear quadrupole moment and a spin I greater than $1/2$. Si^{29} has spin $I = 1/2$ and is thus inactive. $\text{K}^{39, 40, 41}$, Ca^{43} , Fe^{57} , and $\text{Ba}^{135, 137}$ have, however, a spin I greater than $1/2$, but their quadrupole moments are zero or not known at present. O^{17} and Ge^{73} should

[1] Lattice complex = set of equivalent points.

[2] The spectra in this work were obtained by variation of the magnetic field H_0 (The frequency of the hf -field was constant). "Position" thus means the magnitude of the magnetic field in gauss at which the signal appears.

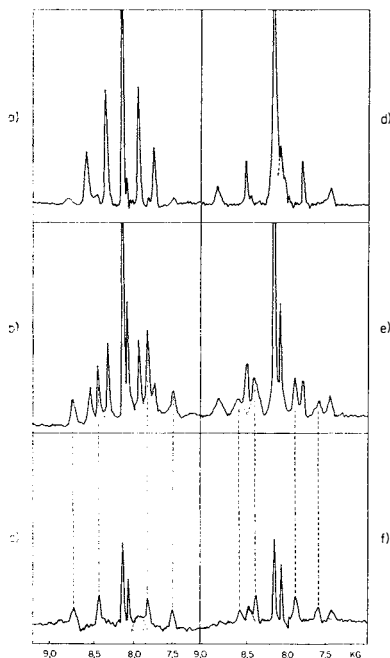


Figure 6. Nuclear magnetic resonance-spectra of Al^{27} and Na^{23} ; (*a+d*) maximum microcline, Hull, Quebec, with appr. 5–10% albite exsolved; (*b+e*) maximum microcline, Perth, with appr. 40% albite exsolved; (*c+f*) albite (low), Amelia. (*a, b, c*) and (*d, e, f*) correspond to different orientations of the crystals with respect to the direction of the magnetic field (for detailed information see Hafner, Hartmann and Laves, 1962). The dotted lines connect the Al^{27} satellites of albite. The dotted peaks are Na^{23} signals. In (*c*) the Na^{23} satellites coincide due to the special orientation chosen, whereas in (*f*) they are resolved.

theoretically show a quadrupole splitting. The concentrations of these atoms are, however, much too small for producing resonance lines to be observable with the available spectrometers.

Figures 6*a-f* show the quadrupole splittings of Al^{27} and Na^{23} of two maximum microclines and of an albite. According to present-day views on the Al/Si-distribution in these substances, five Al^{27} signals in the case of microcline and five Al^{27} and three Na^{23} signals in the case of albite should be expected. This has in fact been found in the case of albite (Figure 6*f*). The albite (low) spectrum proves that Al and Na each occupy only *one* lattice complex in its structure. More complex observations occur in microcline, since microcline in general is twinned

according to the albite and pericline twin laws. For this reason more than five Al^{27} peaks arise. However, considering the twinning (Brun, Hafner, Hartmann, Laves and Staub, (1960)) and, in addition, investigations of a microcline single crystal that became later available (Hafner, Hartmann and Laves, (1962)) gave results analogous to the single crystal of albite. In Figure 6*a* and 6*b* such an orientation of the (twinned) crystal in the magnetic field was chosen that \vec{H}_O was parallel to (010). In this case the signals of all twinned crystal domains should coincide and, therefore only five Al signals occur.

Figure 7*b* shows the spectrum of a maximum microcline which contains much exsolved albite (a small amount of albite is also apparent in figure 7*a*). It is to be noted that the microcline and albite have markedly different quadrupole splitting despite their structural similarity.

In Figure 7*e* the spectrum of a sanidine is presented. It shows only one resonance line, the so-called central signal. The other four lines—the satellites—are broadened to such an extent that they disappear within the background. This broadening results from the disordered Al/Si-distribution in sanidine. Each Al is surrounded by a somewhat different Al/Si grouping and thus has a different environment of electrical charge. Further, the positions of the oxygen atoms differ slightly in various ways. Consequently, innumerable field gradients exist at the sites of the Al ions, the values and orientations of which deviate from each other. As a displacement of the central signal depends only on second order effects, the broadening of the signal is small and is rather expressed by a sharp fall-off in intensity. On the other hand the adularia spectrum (Figure 7*d*) clearly shows satellites, which prove that the Al/Si-distribution is at least partially ordered. The signals are, however, distinctly broadened, the outer satellites even so that they cannot be located.

In Figure 7 the quadrupole splitting of several K-feldspars is compared. The microclines (Figures 7*a, b, c*) exhibit varying degrees of twinning domain size when viewed in the microscope. The intensities of the Al-satellites of the microcline presented in Figure 7*c* are strikingly weak compared to the signals from the exsolved albite (this microcline contains less albite than the one of Figure 7*b*).

This indicates a broadening of the Al signals which should be interpreted as the consequence of an incompletely ordered Al/Si-

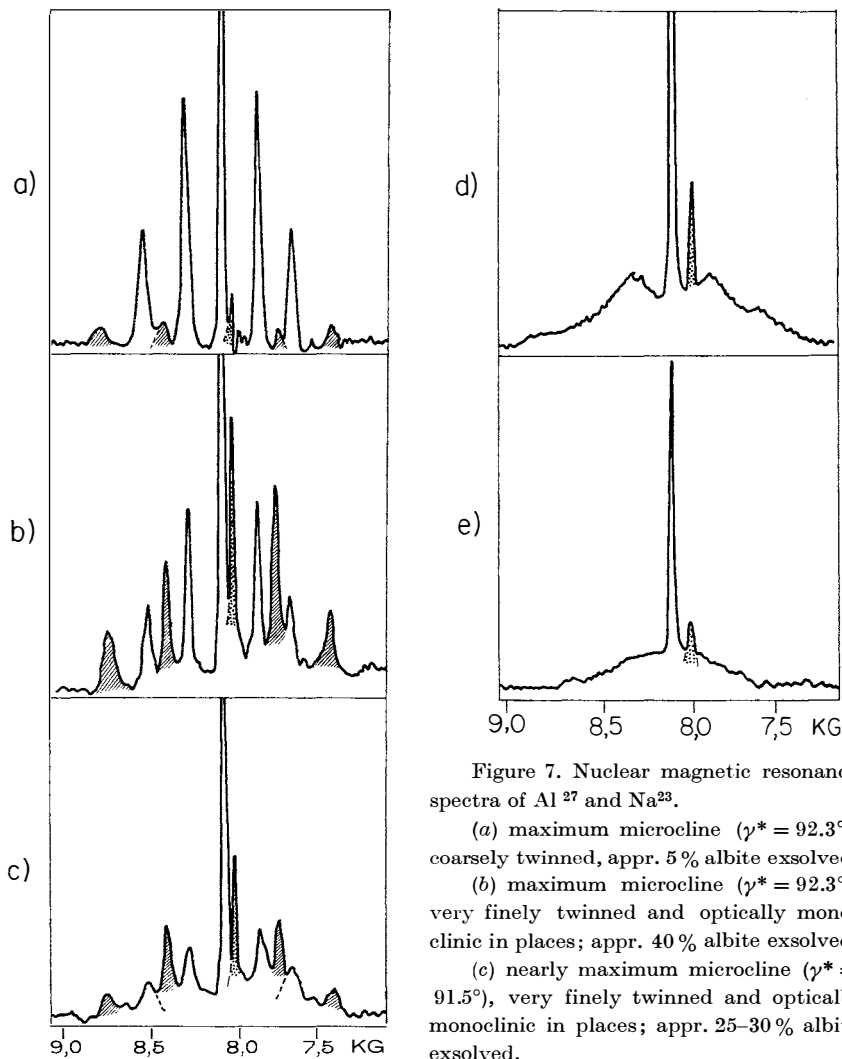


Figure 7. Nuclear magnetic resonance spectra of Al^{27} and Na^{23} .

(a) maximum microcline ($\gamma^* = 92.3^\circ$), coarsely twinned, appr. 5% albite exsolved.

(b) maximum microcline ($\gamma^* = 92.3^\circ$), very finely twinned and optically monoclinic in places; appr. 40% albite exsolved.

(c) nearly maximum microcline ($\gamma^* = 91.5^\circ$), very finely twinned and optically monoclinic in places; appr. 25-30% albite exsolved.

(d) adularia, Disentis; monoclinic, optically and to X-rays; appr. 10% albite in solid solution.

(e) Sanidine, Laacher See, Germany, appr. 11% albite in solid solution (for detailed discussion see Hafner, Hartmann and Laves, 1962).

distribution. In agreement with this conclusion is the fact that the angle γ^* measured by X-rays is less than its maximum value (91.5° instead of 92.3°).

Figure 7d presents for comparison the spectrum of an adularia.

It shows features intermediate between the spectra of the microclines and the sanidine. Hafner, Hartmann and Laves (1962) have shown by extensive measurements on two adularias that the nuclear resonance can best be explained by assuming a very fine domain structure similar to that postulated by Laves (1950) on the basis of the appearance of the diffuse reflections on X-ray photographs. The Al/Si-distribution may be considerably ordered within small individual domains. The distinct broadening of the signals can be correlated with an increase in disorder at the domain boundaries.

Concluding remarks

Infra-red absorption and nuclear magnetic resonance techniques have proved to be very useful in explaining the phase relations amongst the feldspars, where these involve variations in the state of Al/Si order/disorder. Whereas optical and X-ray methods render information only on the average nature of the structure over the entire specimen under investigation, infra-red absorption and nuclear magnetic resonance provide direct information about the environment of a given atomic species. These latter techniques are therefore particularly well suited to give information on the *presence* of order or disorder, especially for the following reasons:

(1) The effects which result from variations in the degree of ordering are quite large, thus allowing rather fine distinctions to be made; (2) In the case of domain structures, the degree of order in the single domains is obtained, whereas X-ray techniques, because of coherence relations, may give an average summation effect which may cause sincere difficulties of interpretation. On the other hand it would be hard to find out with these methods *where* the ordered or disordered elements are located in the crystal structure. In this respect the detailed X-ray work by Bailey and Taylor (1955) on a microcline (intermediate) and by Ferguson, Traill and Taylor (1958) on Na-feldspars, in which order/disorder relations could be inferred from the Al-O and Si-O distances as determined in other silicates (compiled by Smith, 1954), could not be substituted by the kind of work here reported on. Actually, IR-, NMR- and X-ray methods agree very well. To close the circuit Hafner and Hartmann (1962) calculated the magnitude of the field gradients and its orientations relative to the crystallographic

axes of microcline and albite using the atomic positions determined by Bailey and Taylor (1955). and by Ferguson, Traill and Taylor (1958). They compared the calculated field gradients with those derived from the NMR measurements. The agreement is better than could be expected. Thus, the last concluding remark should be: Barth (1934) was right with his ingenious hypothesis.

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