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Brillouin scattering and ultrasonic studies in $K_{1-x}Rb_xAlF_4$: evidence of a new phase

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Abstract. The layered tetrafluoroaluminates $K_{1-x}Rb_xAlF_4$ undergo several structural phase transitions, the existence and features of which evolve when varying x. A study of the temperature variations of the elastic constants derived from Brillouin scattering and ultrasonic experiments is presented for $x = 0.06$, 0.09, 0.12 and 0.15. At room temperature, like in the pure $KAlF_4$ and $RbAlF_4$ compounds, all the mixed crystals studied show $P4/mbm$ symmetry (denoted phase II), differing from the aristotypic phase ($P4/mmm$, phase I) by a tilting of the AlF_6 octahedra around the c axis. Whereas pure $KAlF_4$ presents a unique martensitic-like transition on lowering the temperature, a small amount of Rb^+ ions ($x > 0.02$) induces an intermediate phase ($P2_1/m$, phase IIIa), the existence temperature range of which increases with x. For $x > 0.09$, a new phase ($P2_1/m$, phase IIIb) intercalated between phase II and phase IIIa is evidenced. All the phase transitions are monitored by the softening of normal phonon modes related to the rotation of the AlF_6 octahedra. The measured elastic constants suffer pretransitional and transitional characteristic behaviours that are explained according to the various mechanisms involved during the transformations.

1. Introduction

Numerous compounds of the family of the tetrafluoroaluminates $AAlF_4$ (A=Tl,Rb,K,...) have been extensively studied in recent years using various experimental techniques. Their parent structure is of the perovskite type but presents a layered character owing to the arrangement of the AlF_6 octahedra in sheets disconnected along the c axis and intercalation of the A^+ cations.

$TlAlF_4$ is the historical reference for the so-called 'ideal' or 'aristotypic' high-temperature structure ($P4/mmm$, $Z = 1$), denoted phase I, from which derive all the successive phases encountered when lowering the temperature (Brosset 1937).

In the tetrafluoroaluminates, the microscopic mechanisms of the phase transitions are in most cases relatively well known: rotations of the AlF_6 octahedra around different axes accompanied by softening of vibrational phonon modes and/or branches (Bulou *et al* 1988, Bulou *et al* 1989).

This paper deals with mixed $K_{1-x}Rb_xAlF_4$ compounds, which are of prime importance for the understanding of some peculiar features of the related pure $KAlF_4$ and $RbAlF_4$ crystals, namely those concerning the occurrence of a martensitic-like transition in $KAlF_4$ for which experimental investigation and theoretical interpretation are critical.

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A Raman scattering study of the phases arising in these compounds when varying temperature and concentration x is presented in an accompanying paper (Papin *et al* 1993).

The following is devoted to Brillouin scattering and ultrasonic measurements, which give access to the determination of the elastic constants: their temperature variations near the transitions and sometimes well above are closely related, via their coupling to the normal modes, to the mechanisms responsible for the structural transformations.

A complete elastic study of pure $RbAlF_4$ has been performed previously: starting from the ideal phase I at high temperature, $RbAlF_4$ is subject to a non-ferroic weakly first-order transition at $T_{I-II} = 553$ K leading to a tetragonal ($P4/mbm$, phase II) structure (Bulou and Nouet 1982), the resulting space group being common at room temperature to $RbAlF_4$, to $KAlF_4$ and to the mixed compounds. At lower temperature, $RbAlF_4$ suffers a second-order improper ferroelastic transition ($T_{II-III} = 282$ K) giving rise to an orthorhombic ($Pmmn$, phase III) structure (Bulou and Nouet 1982). Both transitions have been successfully described in the framework of a Landau model, including in the free energy the appropriate order parameters associated with the soft modes (namely M_3 and A_3 at T_{I-II} and X_3 at T_{II-III}) and their coupling with the elastic strains (Debièche *et al* 1990).

As mentioned above, the behaviour of $KAlF_4$ below room temperature is quite different. At $T_{II-IV} = 260$ K a strongly first-order phase transition is observed: it results from the abrupt slipping of the sheets of octahedra (Launay *et al* 1985). The various physical properties related to this transformation evoke a martensitic character. The new phase is monoclinic ($P2_1/m$, phase IV) and the elastic constants are no longer measurable owing to the presence of macroscopic and non-reversible damage in the crystals; the only available elastic information is thus confined to the narrow pretransitional region. On the other hand, the softening of an 'accidentally' flat phonon branch (extending between the M_9 and X_3 symmetry modes) has been evidenced by inelastic neutron scattering above T_{II-IV} (Bulou *et al* 1988): this indicates the presence of a displacive mechanism but a description in terms of a Landau theory nevertheless remains complicated by the very pronounced first-order character of the transformation.

The opportunity for our study of mixed $K_{1-x}Rb_xAlF_4$ compounds arose from the observation of an intermediate phase preceding the martensitic one when substituting a small amount of Rb^+ ions in $KAlF_4$ (Launay *et al* 1987). Moreover the phase diagram reveals for $x > 0.09$ another extra new phase. As will be discussed below, this allowed an unambiguous attribution of the pretransitional effects formerly observed in pure $KAlF_4$ to specific mechanisms peculiar to the new transitions observed in doped crystals and not to the martensitic transition.

2. Experimental protocol and results

The $K_{1-x}Rb_xAlF_4$ crystals ($x = 0.06, 0.09, 0.12$ and 0.15) were grown using the Bridgman–Stockbarger technique from a mixture of AlF_3, KF and RbF in suitable proportions. Although the exact determination of the concentrations is not straightforward owing to gradients in the direction of growth (about 10^{-3} per millimetre), a comparative analysis of the data arising from different techniques revealed a reasonable and coherent evaluation of x for all the crystals studied.

Samples of very good optical quality were cut and polished in appropriate directions according to the imposed selection rules.

The refractive indices were measured at room temperature for all available concentrations.

2.1. Brillouin scattering measurements

Concerning Brillouin light scattering, we present in this paper the results relative to the longitudinal C_{11}, C_{22} and C_{33} elastic constants: they are measured in a standard backscattering geometry using illumination by the 514.5 nm line of a single-mode argon laser. The transverse constants, at least in the orthorhombic phase or quasi-orthorhombic phase, are not available in this geometry.

The scattered light is analysed through a five-pass piezoelectrically driven Fabry–Pérot interferometer: stabilization of the scanning and parallelism of the mirrors is done using a home-made program running on a microcomputer. The finesse and the contrast of the system are typically equal to 55 and 10^8 respectively for our usual experimental procedures of accumulation of the spectra, which can reach a duration of several hours without deterioration of the signal intensity and profile.

The data treatment is also computer-assisted: fits of the Brillouin lines are performed allowing a precise determination of the frequency shift (relative precision around 10^{-3}) as well as the calculation of the linewidths by a deconvolution from the instrumental shape (deconvoluted results are significant for linewidths larger than about 200 MHz).

Cooling of the crystal is obtained by a cryostat using liquid nitrogen or helium, the temperature being regulated within about 0.1 K while the uncertainty upon the absolute value of the sample temperature is estimated as 1 K due to overheating by the laser illuminating power (a few hundred milliwatts).

The temperature variations of C_{11}, C_{22} and C_{33} are reported in figures 1 and 2 for the four studied concentrations.

The notations used to label the elastic constants refer to an orthorhombic approximation for the monoclinic phase: this supposes that monoclinicity is weak, as reasonably supported by our observations and by the results arising from other experimental techniques.

As noticed above, the measurements cannot be performed below the martensitic transformation temperature $T_{\mathrm{III-IV}}$ because of sample breakage. The occurrence temperature of this transformation decreases when x increases, so much so in the case $x = 0.15$ that phase IV is no longer observed when the temperature is lowered down to 4 K.

One of the main features concerning the four concentrations is related to the large 'universal' softening of C_{33} (figure 1) in the tetragonal phase II when the temperature is decreased: the temperature range extension of this softening, already outlined in pure $KAlF_4$, varies with x, as well as its overall amplitude. This softening is steeply interrupted for $x = 0.06$, the following phase (denoted phase IIIa) showing a hardening behaviour down to the martensitic transition. This monoclinic phase IIIa is the first intermediate phase evidenced in the mixed fluoroaluminates. For $x > 0.09$ the pretransitional softening in phase II rejoins continuously the lower-temperature phase C_{33} value: a new additional phase denoted phase IIIb appears, preceding the occurrence of phase IIIa; the signature of the transition at $T_{\mathrm{IIIa-IIIb}}$ is, as for lower concentrations, a marked step but without significant pretransitional softening (see figures 1(*c*) and 1(*d*)).

The situation relative to C_{33} can therefore be summarized as follows. Two intermediate phases between the tetragonal room-temperature and the martensitic phases are observed in $K_{1-x}Rb_xAlF_4$ at high enough substitution x, as indicated in the phase diagram presented in Papin *et al* (1993). The monoclinic phase IIIa, left sided with the martensitic one, is always upper limited by a clearly marked first-order transition (at $T_{\mathrm{IIIa-II}}$ for $x < 0.09$ and $T_{\mathrm{IIIa-IIIb}}$ for $x > 009$). The new phase IIIb (orthorhombic in view of the discussion to follow) arises from phase II via a second-order transition in a continuous way. Finally, the case $x = 0.09$ is the limit of existence for this phase IIIb, for which the splitting of $T_{\mathrm{III-II}}$

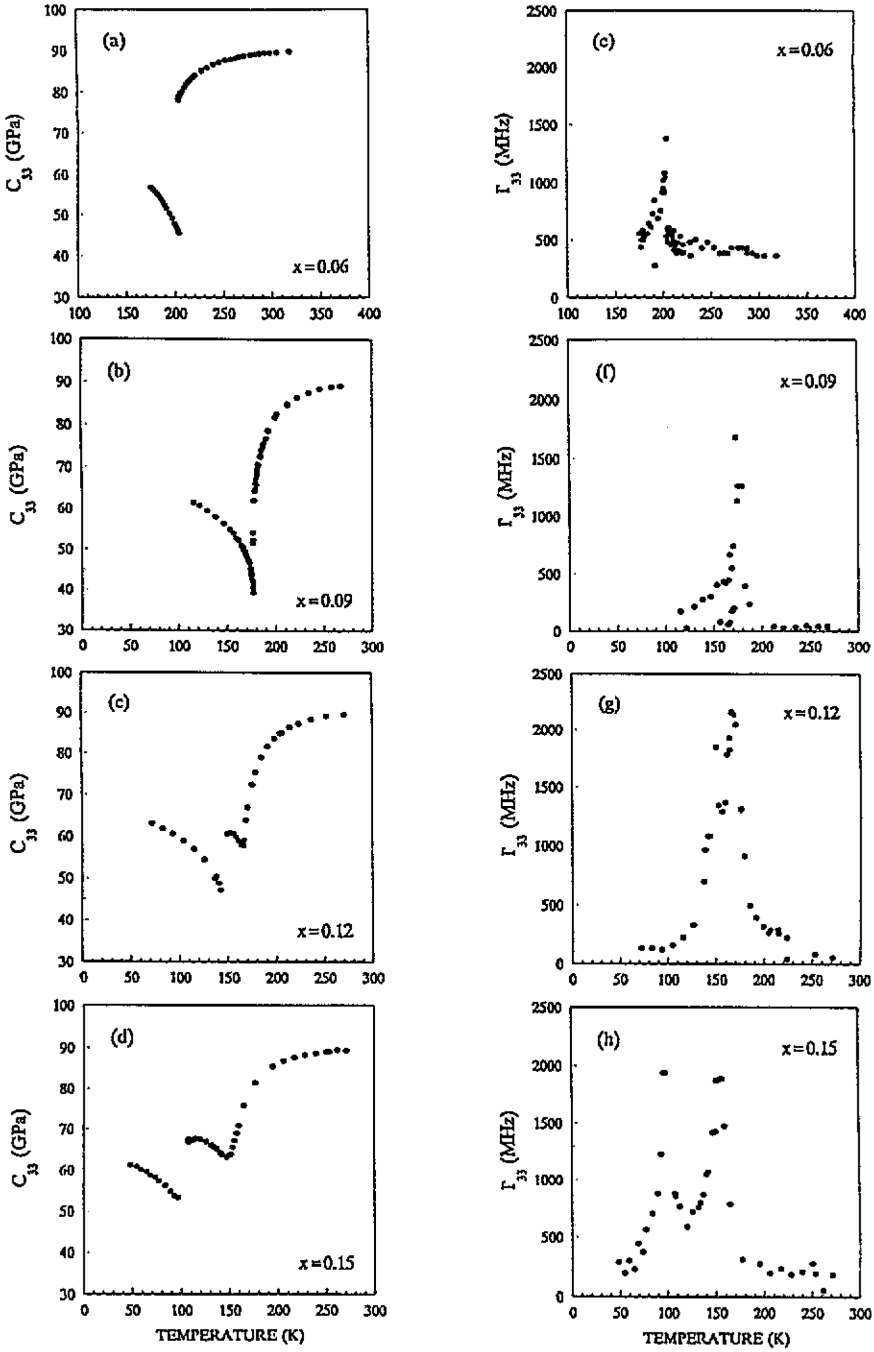

Figure 1. Temperature variations of C_{33} derived from Brillouin scattering measurements in $K_{1-x}Rb_xAlF_4$ for various x concentrations ((*a*) to (*d*)) and the related FWHM Γ_{33} of the Brillouin lines ((*e*) to (*h*)).

is not resolved.

On the other hand, a severe broadening of the C_{33} Brillouin lines is observed around the phase transitions (figures 1(*e*) to 1(*h*)).

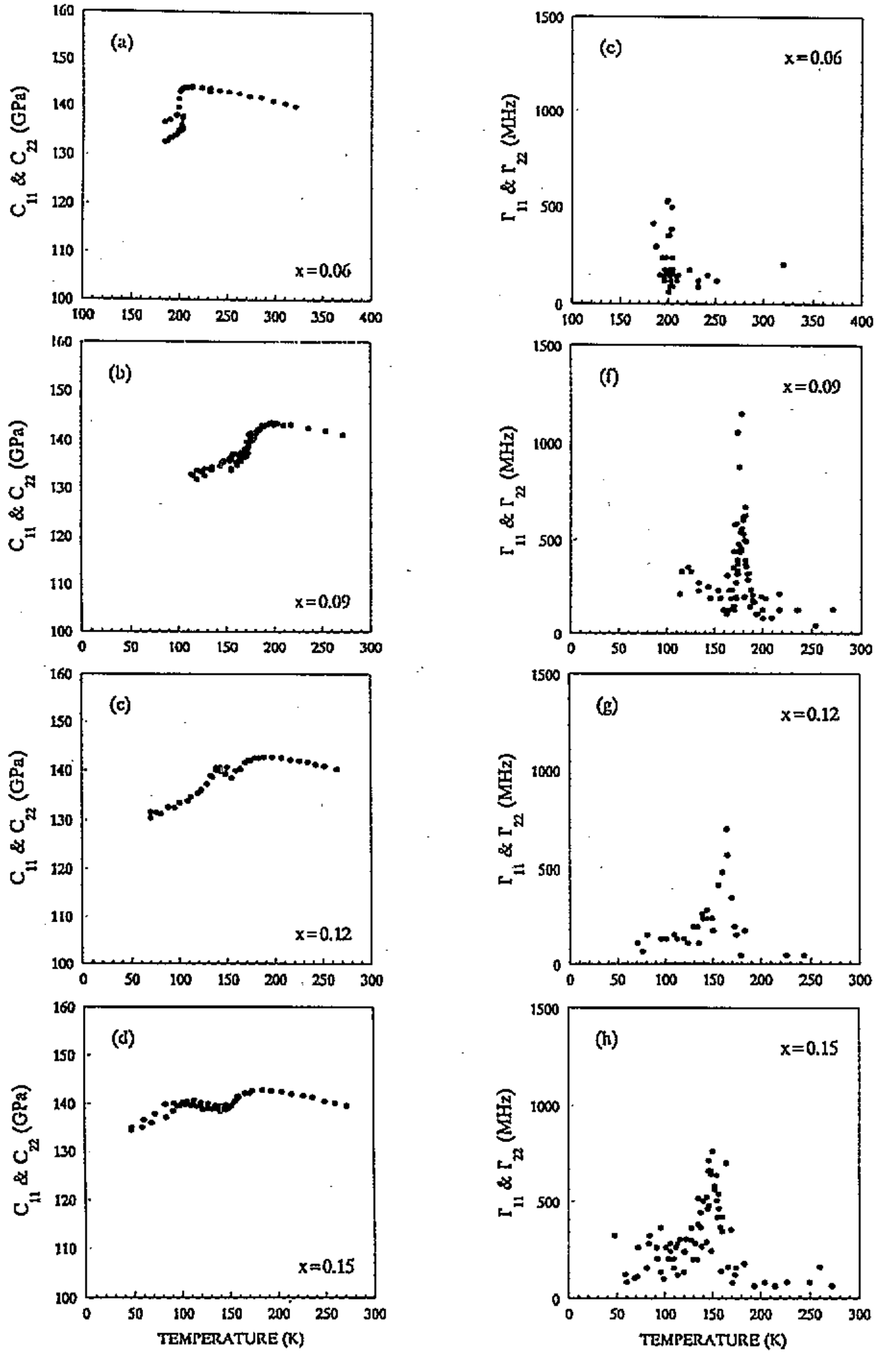

Figure 2. Temperature variations of C_{11} and C_{22} derived from Brillouin scattering measurements in $K_{1-x}Rb_xAlF_4$ for various x concentrations ((*a*) to (*d*)) and the related FWHM Γ_{11} and Γ_{22} of the Brillouin lines ((*e*) to (*h*)).

Let us consider now the C_{11} and C_{22} elastic constants, which obviously do not differ in the tetragonal phase II: their temperature dependences are plotted in figure 2 for the various values of x. Here again results are available down to the martensitic transformation temperature.

Three noteworthy points have to be emphasized: first, the large pretransitional softening observed in phase II upon C_{33} is absent; secondly, the behaviour of C_{11} and C_{22} for all the studied concentrations is characterized by amplitude and slope variations less marked than those exhibited by C_{33}; and thirdly, in the intermediate phase(s) III, C_{11} and C_{22} do not present the same splitting when varying x since it is significant only for $x = 0.06$ and almost negligible at higher concentrations. This latter point has to be related to the sequence of successive phase transitions: for $x = 0.06$, one unique intermediate phase (monoclinic phase IIIa) occurs with a step-like anomaly at $T_{\mathrm{II-IIIa}}$ evoking, as in the case of C_{33}, a first-order character, whereas for $x \geqslant 0.09$ only a smooth slope inversion is observed at $T_{\mathrm{IIIa-IIIb}}$ in addition to the expected continuous downward shift at $T_{\mathrm{IIIb-II}}$.

On the other hand, the low-temperature variations of C_{11} and C_{22} in the region preceding the martensitic transformation (phase IIIa) do not show any hardening like C_{33} but a slight softening down to the breaking temperature of the sample.

Finally, the C_{11} and C_{22} Brillouin lines broaden in the vicinity of the transitions, especially around $T_{\mathrm{II-III}}$ (figures 2(*e*) to 2(*h*)); however the maximum observed widths are smaller than for the C_{33} lines.

To conclude this part, it has to be noticed that a domain structure of the crystals is predicted in phases IIIa and IIIb, respectively monoclinic and orthorhombic. Without anticipating the further discussion, let us mention that, during the light scattering measurements of C_{11} and C_{22}, no splitting or broadening (except obviously near the transitions) of the Brillouin lines could be observed for propagation along a crystallographic direction a or b. When rotating the sample by 90° around the c axis, the respective spectra contain only one phonon line arbitrarily attributed to C_{11} or C_{22}, the occurrence of which depends upon the thermal cycle probably because of residual stresses. As will be developed below this fact is compatible with a distribution in domains and does not contradict related experimental observations from other techniques.

2.2. *Ultrasonic propagation measurements*

The elastic constants in the ultrasonic regime were derived using the pulse-echo-overlap method. The experimental procedure has been described elsewhere. Depending upon the transducers used, longitudinal and transverse sound velocities could be measured around 6 MHz.

We present in figure 3 the temperature variations of C_{11}, C_{33}, C_{44} and C_{66} for the various x concentrations.

Ultrasonic methods are usually more accurate than Brillouin scattering especially for detecting very tiny velocity changes and/or measuring transverse elastic constants. They nevertheless suffer some real handicaps: in our case, the most striking one consists of the failure to propagate ultrasonic waves in the low-temperature phases of our crystals. It is probably related to domain walls developing in the crystals in phases IIIa and IIIb and more destructively in the 'martensitic' phase IV. The results therefore concern the high-temperature pretransitional region (tetragonal phase II).

The information deduced from ultrasonic propagation is not decisive for the investigation of the phase diagram because of these limitations. Anyway in the common region of study, they agree with the Brillouin scattering results and complement them by the determination of transverse elastic constants.

In phase II, the temperature variations of each elastic constant present a common character for all the studied concentrations. The main effects are related to the significant

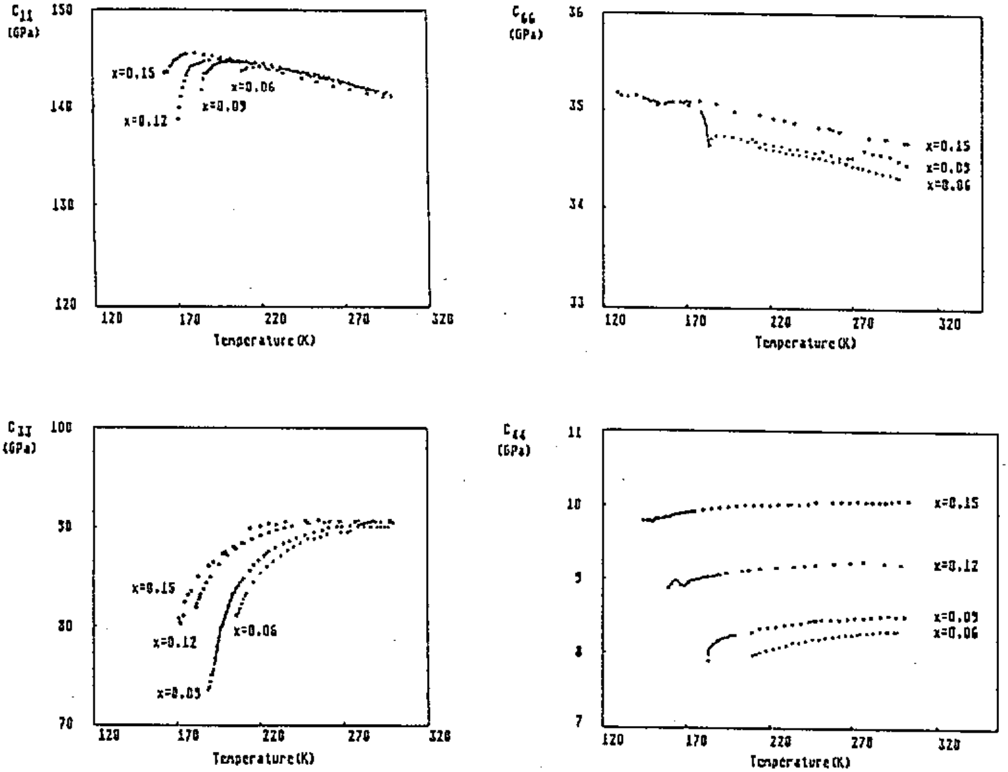

Figure 3. Temperature variations of the C_{11}, C_{33}, C_{44} and C_{66} elastic constants in $K_{1-x}Rb_xAlF_4$ for various x concentrations measured using ultrasonic propagation.

softening, over a large temperature range, of C_{33} and of C_{44} to a lesser extent. On the other hand, no pretransitional anomaly is detected on C_{66}. In the case of C_{11}, the pretransitional softening remains confined close to the phase transition temperature.

3. Discussion

The behaviours of the elastic constants measured in mixed $K_{1-x}Rb_xAlF_4$ show problems of different nature. On the one hand, one is faced with a rich phase diagram: our results complete previous studies using other experimental techniques and show the successively encountered new phases that arise when increasing the rubidium concentration. On the other hand, one has to explain from a homogeneous point of view the mechanisms responsible for the successive phase transitions and for the related behaviours of the elastic constants.

The Raman study presented in the associated paper (Papin *et al* 1993) reveals in detail the phonon spectrum for $x = 0.06$, 0.09 and 0.15. Starting from the aristotypic high-temperature structure $P4/mmm$, the room-temperature structure $P4/mbm$ of $K_{1-x}Rb_xAlF_4$ results from the condensation of mode M_3. At low x concentrations ($x = 0.06$ and 0.09) the unique following intermediate phase IIIa is known to belong to the $P2_1/m$ space group: as previously mentioned the transition is preceded by a softening of a flat M–X phonon branch and can be explained in terms of condensation of the two components of the X_3^1 mode and one component of the M_9 mode. In view of the C_{33} behaviour and of birefringence results (Farhi *et al* 1991), the $T_{\text{II-IIIa}}$ transition is markedly first-order. In a previous paper devoted to the $x = 0.06$ and 0.09 substituted compounds, we described the transition in the framework of a Landau model introducing a free energy development up to the sixth order taking into account only the X_3^1 symmetry mode (Ganot *et al* 1991). It was noticed that the C_{33} shift from phase II at room temperature, well above the pretransitional softening, to phase IIIa just below $T_{\text{II-IIIa}}$ is approximately constant and equal to 45 GPa. On the other hand at $T_{\text{II-IIIa}}$ the birefringence in the (a, b) plane suffers a step from zero (in the tetragonal phase, as expected) to a value independent of x in phase IIIa. This proposed treatment is reasonably supported by these results and is convenient for interpreting the first-order character of the transition. It leads to an orthorhombic approximation for phase IIIa, which is, in some respects, not contradicated by Brillouin measurements.

However, at higher x values ($x > 0.09$), one has to consider the extra phase IIIb intercalated between the phase II and IIIa: its orthorhombic *Pmmn* structure (assumed to in identical to the low-temperature phase III of pure $RbAlF_4$) can be imputed to the condensation of the X_3^1 mode, but the related II–IIIb transition is clearly second-order when examining our elastic constant variations.

Concerning the birefringence in the $(\boldsymbol{a}, \boldsymbol{b})$ plane, its value just below $T_{\text{IIIa-IIIb}}$ as well as its temperature dependence down to the martensitic transition do not differ from the measurements at lower concentrations (Farhi *et al* 1991, Farhi 1992), but indeed a non-zero birefringence exists in the orthorhombic phase IIIb. Notice also that the temperature variations of C_{33} in phase IIIa as well as in phase IIIb depend upon x only weakly and that the abrupt step at $T_{\text{IIIb-IIIa}}$ remains constant when varying x.

We conclude that the state reached by the crystals just below $T_{\text{IIIb-IIIa}}$ and $T_{\text{II-IIIa}}$ is practically independent of the rubidium concentration provided that x is compatible with the existence of phase IIIa.

Another significant result is related to the behaviour of C_{33} above $T_{\text{II-IIIb}}$ or above $T_{\text{II-IIIa}}$: if one proceeds to an appropriate x-dependent translation of the temperature axis, the measured variations fit a universal curve. This temperature translation is immediately related to the x dependence of $T_{\text{II-IIIb}}$, which approaches $T_{\text{IIIb-IIIa}}$ when x decreases: they collapse for $x = 0.09$, the lower concentration limit for phase IIIb to be observed.

On the other hand the overall downward shift of C_{33} between the room-temperature value and the minimum one measured around the second-order tetragonal–orthorhombic transition (i.e. near $T_{\text{II-IIIb}}$) does depend upon x, dereasing from about 50 GPa for $x = 0.09$ to about 30 GPa for $x = 0.15$: such a behaviour could be related to the x varying interval separating $T_{\text{IIIb-IIIa}}$ from $T_{\text{II-IIIb}}$, without contradicting the universal intrinsic nature of the phases IIIa and IIIb when the rubidium concentration increases.

The similarities when studying different concentrations suggest rather simple dependences upon x of the parameters responsible for the involved phase transitions. However a static Landau model would be unable to account for the observed pretransitional variations of C_{33}, which presumably reveal strong effects due to fluctuations. Their interpretation needs to introduce the coefficients that monitor the dynamics and the fluctuations of the order parameters as well as their convenient dependence upon x (see for example Ginzburg *et al* 1983) We are presently working on such a model, which depending upon the numerical values of the parameters that describe it, gives rise to one or two phase transitions in agreement with the experimental results and provides a convenient description of the pretransitional fluctuations.

The last point of the discussion deals with the compared influences of the orthorhombic and the monoclinic distortions in our experimental data. The orthorhombic distortion in phases IIIb and IIIa, which differentiates C_{11} from C_{22}, is clearly evidenced in our Brillouin spectra. Notice that, in figure 2, the labels C_{11} and C_{22} do not refer to well defined absolute values of the ***a*** and ***b*** pseudo-orthorhombic lattice parameters and therefore can be arbitrarily inverted with respect to the two distinct sets of dots. On the other hand, the Brillouin measurements suggest that monoclinic effects in phase IIIa are rather weak. In principle, one mainly expects changes in selection rules arising from additional non-zero elastic constants inducing obliquity of the studied elastic waves and from the occurrence of additional photoelastic coefficients and rotation of the ellipsoid of indices (Ganot *et al* 1989). In our data we did not observe significant variations connected with such possible consequences of monoclinicity. Anyway two distinct monoclinic domains can be directly observed using a polarizing microscope (Farhi 1992): they share a common twofold axis but present opposite monoclinic shear distortions. Since the twofold axis is macroscopically defined, there are not four monoclinic domains in the studied samples, but only two. A complementary birefringence study would certainly be useful in order to confirm these conclusions derived from Brillouin scattering and from microscopic observations.

4. Conclusion

The variations of the elastic constants in $K_{1-x}Rb_xAlF_4$, as deduced from Brillouin scattering and ultrasonic measurements, confirm a phase diagram that is also suggested by other experimental techniques like x-ray diffraction (Brunet *et al* 1991), Raman scattering (Papin *et al* 1993), microscopic observations and birefringence studies (Farhi *et al* 1991, Farhi 1992). As previously discussed (Ganot *et al* 1991) the observed transitions are related to the softening of optical phonon branches describing rotations of AlF_6 octahedra. In the framework of a Landau development of the free energy, it is relatively straightforward to deduce the symmetry of the modes which soften at various points of the Brillouin zone (namely X and M) and to build an appropriate expression of this potential, which contains two coupled order parameters and gives rise to the observed transition or sequence of transitions. We have experimentally shown some quantitative or at least semi-quantitative invariants in the behaviour of the elastic constants when the rubidium concentration is modified. On the other hand, we have observed strong pretransitional effects, which derive from the dynamics and from the fluctuations of the order parameters. For any given concentration, it is relatively easy to take these effects into account and to fit the experimental results with an appropriate model. Concerning the influence of x, it is clear that when increasing x the phase sequence arising in $RbAlF_4$ is favoured: however, a deeper and more quantitative understanding of the concentration dependence of the properties of the mixed crystals has still to be sought. From an experimental point of view they could be helped by further Raman and, if possible, neutron scattering measurements, by the Brillouin study of the variations of the transverse elastic constants and by additional birefringence results. Finally, since it has been proved that in most cases the orthorhombic orientation does not depend upon position inside the studied sample whereas the monoclinic distortion reverses from place to place, given rise to the random occurrence of two distinct types of monoclinic single domains, various experimental studies under an applied uniaxial stress would be useful in order to understand the driving forces for the formation of domains.

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