PHYSICAL REVIEW B VOLUME 21, NUMBER 3 1 FEBRUARY 1980

Neutron scattering study of the one-dimensional ionic conductor β-eucryptite

W. Press
Institut für Festkörperforschung der Kernforschungsanlage Jülich, 5170 Jülich, Federal Republic of Germany

B. Renker
Institut für Angewandte Kernphysik I, Kernforschungszentrum Karlsruhe, 7500 Karlsruhe, Federal Republic of Germany

H. Schulz
Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80, Federal Republic of Germany

H. Böhm
Mineralogisches Institut der Universität Münster, 4400 Münster, Federal Republic of Germany

(Received 20 June 1979)

The phase transitions in β-eucryptite have been investigated by the slow neutron scattering technique. In the temperature range $430 \leqslant T \leqslant 490\,^{\circ}\mathrm{C}$ an incommensurate structure is found which coexists with the well-known low-temperature superstructure in the range $430 \leqslant T \leqslant 482.5\,^{\circ}\mathrm{C}$. A pronounced temperature dependence of the satellite positions is observed. Interpretations of the observed scattering are based on a simple model which accounts only for the Li chains within the quartz channels. The width of the diffuse scattering at 525 °C indicates that the Li correlations within a chain are effective over 19 ± 3 Li-Li distances while chain-chain correlations are relatively weak. A rather profound analogy to the triangular Ising lattice in the presence of an external field is discussed. At present this model does not explain the incommensurate structure.

I. INTRODUCTION

Recently a pronounced one-dimensional character of the ionic conduction in β-eucryptite (β-$\mathrm{LiAlSiO_4}$) has been reported.[1,2] The Li conductivity along the hexagonal axis ($\sigma_{\parallel}$) is about 3–4 orders of magnitude larger than the one in the a-b plane ($\sigma_{\perp}$) and reaches a value $\sigma_{\parallel} \cong 0.1\ \Omega^{-1}\,\mathrm{cm}^{-1}$ at a temperature $T = 600\,^{\circ}\mathrm{C}$. The high mobility of the Li^+ ions is connected with the following structural properties[3–9]: the Li^+ ions are aligned along chains in the so-called quartz channels and two possible sites are available for each Li^+ ion of tetrahedral oxygen coordination.[3,4] An Arrhenius-type of temperature dependence for the conductivity remains almost unaffected by an ordering transition at about 490 °C.[10] This phase transition, which seems to be almost continuous, by itself represents an interesting phenomenon. The present neutron scattering study was performed with a rather limited energy resolution $\Delta E \simeq 1$ meV (full width at half maximum) and for this reason no final answers pertaining to the ionic conduction could be obtained. The experiments, therefore, concentrated on the phase-transition aspect of β-eucryptite.

In this context it is necessary first to review some of the structural properties of $\mathrm{LiAlSiO_4}$ which have been investigated with x rays[3–8] and, very recently, with neutrons.[9] The high-temperature structure of $\mathrm{LiAlSiO_4}$ (space group $P6_222$) bears close resemblance with the one of high quartz (β-$\mathrm{SiO_2}$).[7] A difference concerns the arrangement of Al and Si, which order in layers perpendicular to the c axis and cause the c axis in β-$\mathrm{LiAlSiO_4}$ to be doubled with respect to quartz. The charge deficiency caused by introducing Al into the quartz framework is compensated by the Li^+ ions, which, as mentioned above, occupy positions in the "quartz channels". The recent neutron-diffraction work by Guth and Heger[9] showed that the two possible Li positions at 000 and $00\frac{1}{6}$ are not occupied at random. A 68% probability is found for positions 000 (sheets of Si), while the corresponding value for positions $00\frac{1}{6}$ (sheets with Al) is 22%. Ten percent of the positions are not occupied.[9] At low temperatures the Li ions form an ordered arrangement. Twenty-five percent of the Li ions occupy sites $00\frac{1}{6}$ which are coplanar with the Al ions, while 75% are located at the alternative 000 sites coplanar with the Si ions.

It has been suggested, that the phase transition mainly involves an ordering of the Li ions in their respective chains and a phase locking of neighboring chains.[4–7] We believe that this indeed is an important aspect of the phase transition, on which models describing the transition could be based. There are, however, also features reminiscent of the high quartz to low quartz transition. That means, the phase transition not only involves an ordering of Li chains, but is accompanied by a distortion of the $\mathrm{AlSiO_4}$ framework. This distortion can be looked upon as rotations of interconnected AlO_4 and SiO_4 tetrahedra and has the character of a displacive transition, while the Li ordering rather has the character of an order-disorder transition. The rotations of SiO_4 tetrahedra at the Γ-point transition in quartz have been discussed in detail by Megaw[11] as well as by Grimm and Dorner.[12] In β-eucryptite the situation is more complex as the transition occurs at the *M* point and hence involves a doubling of both the hexagonal *a* and *b* axis. Due to uncertainties connected with the low-temperature structure of β-eucryptite a detailed analysis of the mode(s) in the high-temperature phase which are principally involved in the transition will not be attempted here. There is no experimental evidence of deviations from hexagonal symmetry.[4,6,9] However the absence of an extinction rule for reflections $(00l)$[9] in conjunction with the possible subgroups of the spacegroup $P6_222$,[13] suggests a crystal class of lower symmetry.

In the present neutron scattering experiment the following aspects have been studied: (i) a preliminary attempt has been made to directly observe the diffusion of the Li^+ ions by incoherent neutron scattering and to investigate effects of the high ionic mobility on the phonon dispersion. (ii) The main concern of this work is the phase transition at $T_1 = 490\,°C$.

II. EXPERIMENT

Large single crystals containing natural Li have been grown by the flux method, described elsewhere.[14] Experiments were performed with a crystal of 1.2 cm^3 volume, mainly in the $(h0l)$ zone oriented in the scattering plane. The sample mosaic was determined to be less than 10^{min}.

Neutron scattering experiments were done on a triple-axis spectrometer at a thermal beam tube of the FRJ2 reactor in Jülich. Pyrolytic graphite crystals were used both as monochromators, analyzer and also as a filter in order to remove the higher-order contamination in the monochromatic beam. 45^{min} collimators were employed for most experiments. At an incoming energy $E_i = 14.7$ meV the energy resolution ΔE was about 1 meV, thus permitting only preliminary dynamical measurements. For intensity reasons no attempt has been made to improve the instrumental resolution.

III. DYNAMICS

Li is a relatively weak scatterer for neutrons: $\sigma_{inc} = 0.42$ barns[15] and $\sigma_{coh} = 0.57$ barns.[16] Its incoherent scattering cross section, however, is about an order of magnitude larger than the sum of all incoherent scattering cross sections of the other atoms in a formula unit of $LiAlSiO_4$. Despite the limited resolution an attempt has been made to resolve the energy width $\Gamma(Q)$ (half width at half maximum) of the quasielastic scattering; here Q is the momentum transfer of the neutrons. The energy width $\Gamma(Q)$ can be related to a diffusion constant D, which in turn can be compared with the ionic conductivity. Further it may be hoped to learn about the geometry of the stochastic jumps[17] as well as about the question of correlated motions of the conducting ions.

Inelastic neutron scattering experiments have been performed at several Q values ($0.6\ \text{Å}^{-1} < |\vec{Q}| < 4\ \text{Å}^{-1}$), both along $[00l]$ and perpendicular to this direction. Measurements at $T = 20$ and $550\,°C$ show that elastic intensities at $Q \simeq 4\ \text{Å}^{-1}$ decrease by roughly a factor of 2 and the background increases strongly when heating to 550 °C. Least-squares fits of the spectra did not yield any evidence of a quasielastic contribution to the elastic line (related with the conduction mechanism) nor could we identify a broad quasielastic component, as has been seen in α-AgI,[18] representative of a local diffusive motion of the conducting ions and not contributing to the conduction. Further measurements require much better resolution and are planned with a single crystal with the isotope ^7Li.

With a conductivity $\sigma_{\parallel} \cong 0.1\ \Omega^{-1}\,cm^{-1}$ which has recently been reported,[1,2] a linewidth $\Gamma(Q = 1\ \text{Å}^{-1}) \simeq 0.1$ meV may be expected, for completely uncorrelated motion. However, the one-dimensional conduction within the "quartz channels" provides a somewhat pathological example for ionic conduction and a highly correlated motion seems likely. Such correlation effects (often expressed in terms of a "correlation factor") will cause that both quantities $D(T)$ and $\Gamma(T)$ are smaller than to be expected from the Nernst-Einstein relation.

Additionally acoustic phonons with energies below 10 meV have been measured at two temperatures (20 °C, 550 °C) in directions $[\zeta 00]$ and $[00\zeta]$. No broadening of the phonon groups at high temperatures has been observed, in difference to the findings in PbF_2,[19] and the dispersion is quite normal. Only a usual temperature softening of all phonon energies by about 10% was found.

IV. PHASE TRANSITION AND MODULATED STRUCTURE

A. Initial findings

In order to learn about the temperature dependence of the superlattice intensities and of the critical scattering in the vicinity of the phase transition, rather extensive measurements in the (010) zone of

$LiAlSiO_4$ were made at various temperatures. Scans along [ζ00], [00ζ] and constant-Q scans were done mainly around zone-boundary points $h/2\ 0\ l$ with both h and l odd [indexing with the high-temperature cell $a(550\,°C)=5.27$ Å and $c(550\,°C)=11.06$ Å] which become the so-called a reflections in the ordered low-temperature phase.[8] Additionally a few main reflections $h0l$ (present also above 490 °C) and zone-boundary points $h/2\ 0\ l$ with l even have been sampled. As reported in previous x-ray analyses,[3–8] the latter reflections are found to be rather weak. The most prominent result is the finding of an intermediate modulated structure below the phase transition, which we observe within a temperature range $T_2=430\pm5\,°C$ to $T_1=490\pm2\,°C$. Figure 1 shows scans $(1.5\pm\zeta,0,\bar{\zeta})$ with the analyzer of the triple-axis spectrometer set to the elastic position. Three typical temperature regimes may be distinguished.

(i) Above T_1 [Fig. 1(b)] we observe pronounced diffuse scattering along the direction [ζ00] which connects main reflections. From previous x-ray measurements and our own measurements (some of which are shown in Fig. 2) we know that this diffuse scattering appears within sheets, which means correlations along chains (parallel to the c axis) in direct space. There is, however, a well-defined $\vec{Q}$ dependence of the diffuse intensity perpendicular to the

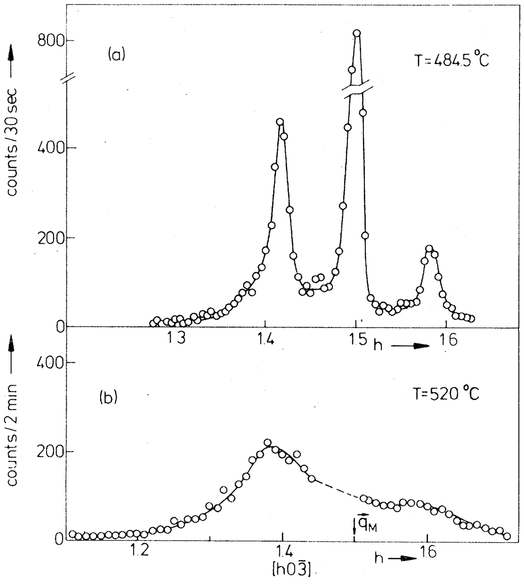

FIG. 1. Two elastic scans with a triple-axis spectrometer along the $[h0\bar{3}]$ direction of a β-eucryptite single crystal: (a) A measurement just below $T_1=490\,°C$ demonstrates the appearance of both a superlattice peak (connected with an M-point distortion) and a consequent doubling of the cell constant a and two satellite peaks (indicating a modulated phase). (b) Shows the peaking of the diffuse scattering at the satellite positions above the transition temperature T_0.

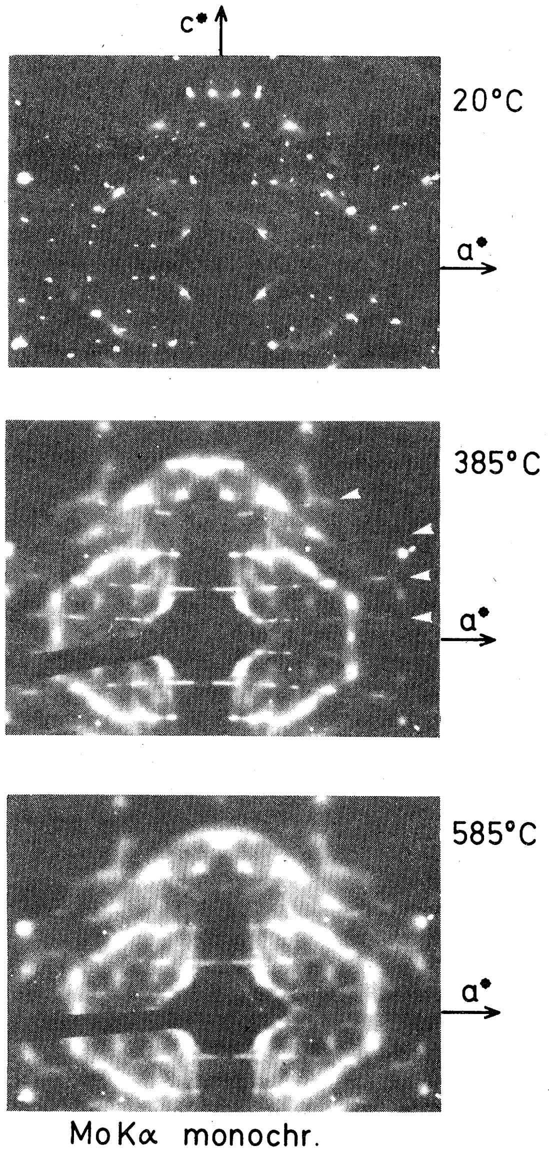

FIG. 2. Photographs taken with fixed film, fixed crystal, and monochromatic Mo $K\alpha$ radiation. Orientation of the crystal and investigation temperature are marked in the figure. The diffuse intensities at 385 and 585 °C in the form of very broad lines are caused by thermal diffuse scattering. The diffuse intensities in form of narrow lines parallel to a at $l=1,3,5,7$ (marked by white arrows at the 385 °C photograph) are caused by the one-dimensional ordering of the lithium ions in the structural main channels. These lines are generated by the so called a reflections (see text), which become more and more diffuse perpendicular to the c axis, e.g., the three-dimensional ordering is reduced more and more. These lines become broader also parallel to c at 585 °C. From the broadness parallel to c follows a correlation length of approximately 10 Li-Li distances per ordered chain.

chain direction—visible both in the neutron spectra and on the x-ray photographs. It is due to correlations between different chains and as such becomes weaker when the temperature is increased far above the transition temperature T_1.

(ii) Below the chain ordering temperature $T_0 \cong T_1$ superlattice reflections appear at the zone boundary M points of the high-temperature phase. Almost simultaneously, probably at a slightly higher temperature, satellite peaks appear at $(1.5 \pm \delta, 0, \bar{3})$ with $\delta \simeq \frac{1}{12} a^*$ [see Fig. 1(a)] and at symmetry related positions. No satellites are observed at positions 2δ and 3δ nor do we find satellites around the main peaks. The absence of higher-order harmonics indicates a sinusoidal modulation of occupation numbers. We may conclude that there is a modulation of the Li chain occupation probability with a modulation wave vector perpendicular to the c direction. The intensity of all observed satellite pairs is rather asymmetric. For this reason the simple picture of a sinusoidal modulation only of the Li chain occupation does not yield a complete explanation. Another remarkable finding concerns the fact that the diffuse scattering is maximal at the satellite positions, while no critical scattering seems to be directly connected with the appearance of superlattice peaks.

(iii) Below $T_2 = 430 \pm 5$ °C the satellites disappear. Only superlattice peaks remain and continue to grow in intensity with decreasing temperature.

B. Results obtained from least-squares fits

In order to obtain more quantitative information least-squares fits of the observed spectra were performed. With one exception no complete four-dimensional resolution corrections have been applied. This would have required much more complete measurements in $\vec{Q}$-ω space. Therefore peak intensities as well as linewidths shown in Fig. 3 only have qualitative character. As it turns out, however, the energy width of the diffuse scattering must be well below our energy resolution $\Delta E = 1.0$ meV even at the highest attained temperatures. The following results are obtained:

(i) Disordered phase ($T \gtrsim T_1 = 490$ °C). As may be seen in Fig. 4 the intensity of the diffuse scattering strongly increases on approaching the phase transition. Although the transition appears to be smooth in the present measurements (Fig. 3), a decision as to whether this transition really is of second order would require resolution corrections. Only then an extrapolation of the inverse susceptibility $\chi^{-1}(\vec{Q} = \vec{Q}_M \pm \vec{\delta}\,) \sim I^{-1}$ to a temperature below T_1 would provide the prove for a (probable) first-order character of the transition. The $\vec{q}$ width of the diffuse intensity in the direction of c^* is larger than obtained when convoluting a scattering law $S(\vec{Q}, \omega) \sim \delta(Q_z)\delta(\hbar\omega)$ with the experimental resolution. We may ask, whether this is due to a finite energy width of the scattering function or due to finite spatial correlations within the Li chains. An answer may be based on the x-ray photograph at 585 °C which indicates a q width corresponding to correlations over about 10 Li ions along the chain direction. Additionally constant Q scans (energy is scanned) and constant energy scans (with $\hbar\omega = 0$ and Q_z scanned) at 520 °C have been analyzed. For this purpose a four-dimensional convolution of the resolution function of the triple-axis spectrometer and the above

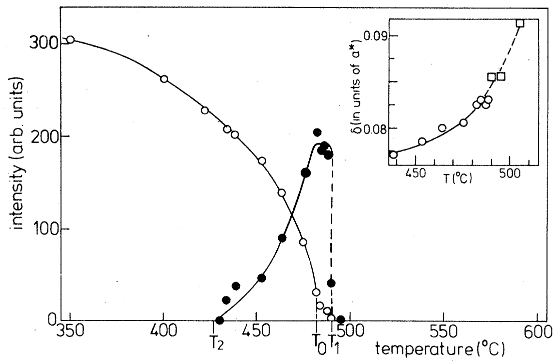

FIG. 3. Intensity of both the superlattice peak [$(30\bar{3})$, open circles] as well as of the satellite peaks [$(3 \pm \delta\ 0\ \bar{3})$, full circles] are shown. In the temperature regime $T_2 = 430$ °C $\leq T \leq T_1 = 490$ °C incommensurate structures are observed. A power law fitted to the superlattice intensity yields a transition temperature $T_0 = 482.5$ °C (with ommission of two data points which are probably due to a rounding of the transition) which suggests the existence of a narrow phase with a modulation but no commensurate superstructure. The insert depicts the satellite position (squares relate to the disordered phase $T \geq T_1 = 490$ °C).

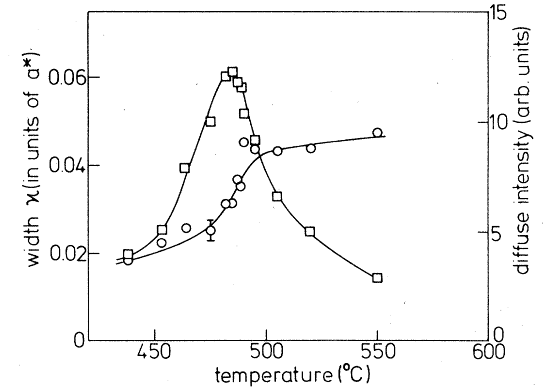

FIG. 4. Shows both the peak intensity (open squares) of the diffuse scattering and the q width of Lorentzians κ (open circles) fitted to the diffuse scattering (as, e.g., in Fig. 1).

scattering law with one of the δ functions replaced by a Lorentzian has been performed. The assumption of a finite energy width fails to provide a consistent fit of both scans. One can, however, fit the experimental data when replacing $\delta(Q_z)$ by a Lorentzian of half width $\kappa_{\parallel}$. An inverse correlation length $\kappa_{\parallel}(520\,^{\circ}\mathrm{C}) = 0.014 \pm 0.002$ Å^{-1} is obtained, which corresponds to correlations over 19 ± 3 Li-Li distances. One may conclude from both the neutron and the x-ray measurements that the picture of infinitely long Li chains only provides an approximate description of the real situation. It will become worse at higher temperatures, as the ionic conductivity increases—but correspondingly should be more adequate at lower temperatures. Correlations within the *a*-*b* plane are much more short ranged (Fig. 4). Above $T_1 = 490\,^{\circ}\mathrm{C}$ the finite Q resolution can be ignored and a correlation length of about $2a$ is found. At temperatures much above T_1 chain-chain correlations (of site occupations) probably can be ignored and the diffuse scattering will provide information pertaining both to the geometry and the time scale of the diffusion mechanism even by coherent scattering.

It is somewhat surprising that the linewidth $\bar{\kappa}_{\perp}$ (half width at half maximum; not resolution corrected) of the diffuse scattering seems to decrease monotonously even below the phase transition (Fig. 4). The origin of this is probably the following: within our simple Li-chain model diffuse intensity occurs only in planes perpendicular to the *c* direction and labeled by $Q_z = 3nc^*$ with n odd. In absence of chain-chain correlations the diffuse intensity within a plane is constant. The observed modulation of the intensity has been attributed to the "chain ordering mode" which leads to the modulated structure below $T_1 = 490\,^{\circ}\mathrm{C}$. There are, however, other "chain ordering modes" which are noncritical and which may be responsible for the observed temperature dependence.

(ii) Modulated phase(s) ($430 \leq T \leq 490\,^{\circ}\mathrm{C}$). The spectra recorded at $430 \leq T \leq 490\,^{\circ}\mathrm{C}$ have been fitted with a five-peak structure: (i) Three Bragg peaks, Gaussians with about the same Q width (determined by the instrumental resolution) for the superlattice peak and the pair of satellite peaks; and (ii) two Lorentzians located at the satellite positions and with identical but temperature-dependent Q width. Above $T_1 = 490\,^{\circ}\mathrm{C}$ there are no Bragg features in the vicinity of an M point and below $T_2 = 430\,^{\circ}\mathrm{C}$ the satellite intensity vanishes. The contribution of a powder peak originating from the aluminum sample container has been subtracted.

Figure 3 shows the results connected with the Bragg components of the spectra. We may note, that the satellite position is strongly temperature dependent (see insert in Fig. 3). This is a finding also in many other systems with phase transitions into incommensurate structures (see, e.g., Refs. 20–22). We have included some data points from the disordered high-temperature phase. There δ reflects the position of the two Lorentzians fitted to the diffuse intensity. It decreases from $\delta = 0.11a^*$ at 550 °C to $\delta = 0.078a^*$ at 430 °C. At $430 \pm 5\,^{\circ}\mathrm{C}$ a lock-in transition to $\delta = 0$ is observed; the amplitude of the modulation with wave vector $\vec{q} = (q_M \pm \delta, 0, 0)$ drops to zero at this temperature.

Over a wide temperature range satellites and superlattice peak appear simultaneously. There is some similarity with the para- to ferroelectric phase transition in $\mathrm{NaNO_2}$: there the modulated phase and the ferroelectric phase coexist as well, however in a much narrower temperature range.[23,24] In case of $\mathrm{NaNO_2}$ the modulated phase appears before the Γ-point distortion occurs, when cooling from the paraelectric phase. At the first glance this seems to be different in β-eucryptite: Satellites and superlattice peaks seem to show up at the same temperature, namely, $T_1 = 490\,^{\circ}\mathrm{C}$. We have attempted to explain such a behavior with a Landau theory with one of the distortions as the primary order parameter and the other one as a secondary order parameter, however, unsuccessfully. In particular it is very difficult to relate the almost continuous increase of the superlattice intensity with the steep increase of the satellite intensity.

We now believe that there are two successive transitions separated by about 7–8 °C only. A first transition at $T_1 = 490\,^{\circ}\mathrm{C}$ which is concerned with the formation of the modulated phase and at $T_0 = 482.5\,^{\circ}\mathrm{C}$ a second transition at the M point which causes a doubling of the cell constant a. The above finding is somewhat obscured by the "rounding" of the superlattice intensity around T_0. Such a behavior is not a well understood but rather frequently observed feature also in other systems. Judging from the temperature dependence of the Bragg intensities (of the satellites) the transition at T_1 appears to be of first order, whereas the one below looks continuous or almost continuous (with respect to both the superlattice and the satellite intensities).

(iii) Low-temperature phase ($T \leq T_0 = 482.5\,^{\circ}\mathrm{C}$). Below $T_2 = 430\,^{\circ}\mathrm{C}$ the satellite peaks disappear and only the superlattice peaks of the low-temperature phase remain in addition to the Bragg peaks of the high-temperature phase. There is no anomalous behavior of the temperature dependence of the superlattice peaks in the vicinity of T_2.

The observed superlattice intensities have been fitted with a power law $I \sim (T_0 - T)^{2\beta}$ as is usually done at second-order phase transitions. It turns out that a power law only can be successfully fitted if two data points in the immediate vicinity of T_0 are omitted from the fit. The rounding of the transition due to this finite intensity may be caused by temperature gradients, inhomogenities in the sample, etc. An exponent $\beta = 0.22 \pm 0.01_5$ is obtained. This value is smaller than what is usually observed at second-order phase transition in three-dimensional systems. There are several possible explanations [e.g., presence of a tricritical point: $\beta=\frac{1}{4}$; two-dimensional Ising system (as discussed later): $\beta=\frac{1}{8}$]. We would like to add another explanation, namely, that small β values often result, if data in the vicinity of a phase transition which ultimately is discontinuous are fitted by a power law. What is important, though, is a resultant phase transition temperature $T_0=482.5\pm1.0\,^\circ\mathrm{C}$ which supports the conclusion that there are two successive phase transitions at $T_1=490\,^\circ\mathrm{C}$ and $T_0=482.5\,^\circ\mathrm{C}$.

V. CONCLUSIONS

It is tempting to investigate the observed phase transitions on the basis of the Li-chain system only. In the substance $Hg_{3-\delta}AsF_6$, which can be viewed as a solid consisting of mercury chains embedded into a AsF_6 framework,[25,26] the atoms within the mercury chains have no well-defined positions with respect to the framework. This is different in β-eucryptite. If we ignore the finite correlation length in the direction of the hexagonal c axis, the high-temperature phase of β-$LiAlSiO_4$ can be looked upon as consisting of infinitely long Li chains (Li-Li distance equal to $\frac{1}{3}c$) with two alternative positions: chains of type 1 start at 000, while chains of type 2 start at 0 0 $\frac{1}{6}c$. At this point we may describe the chains by Ising spins, e.g., type-1 chains as up spins and type-2 chains as down spins and obtain an equivalence between the idealized chain system (space group $P6/mmm$) and the triangular Ising lattice.

Obviously the high-temperature phase is disordered (paramagnetic). Concerning the low-temperature phases a problem remains: Either one is faced with a distortion connected with a single Γ-M direction (single $\vec{q}$ state) and the hexagonal symmetry is apparent only because of domain averaging, or the symmetry really is hexagonal and the distortion is connected with a star of three equivalent q vectors (triple $\vec{q}$ state).

A commensurate triple $\vec{q}$ state and modes within the $\hat{\tau}_1$ representation (in the notation of Kovalev[27]) lead to the space group $P6/mmm$ with a doubled unit cell for the Li-chain system and, equivalently, to $p6m$ for the triangular Ising lattice. Despite some problems with forbidden reflections,[9] structure analysis so far has adopted the triple $\vec{q}$ state and we shall do the same in the following. The fully ordered low-temperature phase then corresponds to a ferrimagnet (Fig. 5) with three spins up and one spin down.

Phase transitions on the triangular Ising lattice have recently been studied by the Monte Carlo technique.[28,29] Interactions between nearest neighbors (J) and next-nearest neighbors (J') have been included as well as an external field. With an antiferromagnetic interaction (J and $J'<0$) and zero field, the system does not display a phase transition. In the presence of a sizable external field, however, a transition to a ferrimagnetic phase, as described above, occurs.

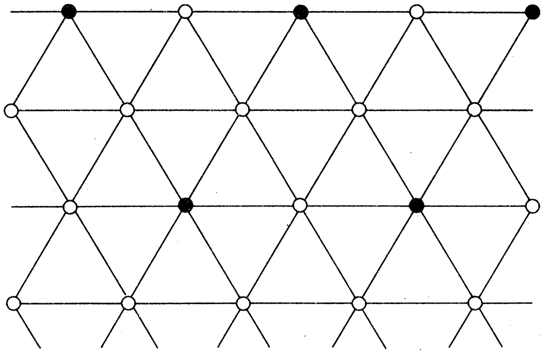

FIG. 5. "Ferrimagnetic order" on a triangular Ising lattice is illustrated which also reflects the chain ordering in the low-temperature phase. Open and full circles correspond to the two possible spin (chain) configurations.

As it turns out all necessary conditions for the occurence of a ferrimagnetic ordering on the triangular lattice are qualitatively fulfilled in β-eucryptite.

(i) First, the Coulomb interaction between chains consisting of Li^+ ions indeed yields an antiferromagnetic interaction, irrespective of the distance between two interacting chains.

(ii) Concerning the external field we have to remember that the percentage of up spin in the disordered phase is about three times higher than that of the down spins.[9] This is in accordance with symmetry, as it does not relate type-1 and type-2 sites (primary and secondary channels, respectively) in β-$LiAlSiO_4$. Li atoms at $z=\frac{1}{6}c$ are located in layers of Al neighbors, while Li atoms at $z=0$ are within layers of Si. Now the Si-O bond length in a SiO_4 tetrahedron is about 0.13 Å smaller than the Al-O bond length in a AlO_4 tetrahedron, causing less steric hindrance and consequently a deeper potential well for the Li atoms in the silicon sheets. The difference in this interaction certainly does not fix the ratio of Li ions at the two different sites at 3:1 in the high-temperature phase, but definitely off sets it from a distribution with equal weight for spin up and spin down. Thus it plays the role of a crystal field (equivalent to an external field) which favors the occupation of positions in the Si sheets and hence provides one of the necessary bases for a "ferrimagnetic" ordering.

Unfortunately the consideration of the triangular Ising lattice does not include the possibility of spatial inhomogeneities and a resultant incommensurate phase. An extension of the theoretical work along

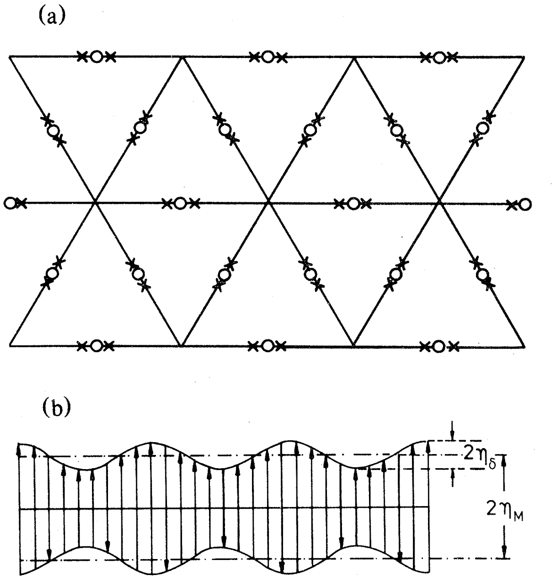

FIG. 6. (a) Appearance of superlattice and satellite peaks, e.g., in the $(hk3)$ plane. (b) Illustration of the modulation of the chain occupation probability in the regime $T_2 \leq T \leq T_0$, in which satellite and superstructure peaks coexist η_M denotes the amplitude of the commensurate modulation and η_δ denotes the amplitude of the incommensurate modulation.

these lines seems to be very desirable. What remains to be explained, either on the basis of a Landau free energy or within the Ising model using Monte Carlo techniques is (i) the sequence of phase transitions and (ii) the critical scattering only peaking at the satellite positions. The main problem with the various phases is the coexistence of a commensurate and an incommensurate phase in the regime $430 < T < 482.5\,^\circ\mathrm{C}$ [Fig. 6(a)]. In this regime even the description of the chain occupation number $n(\uparrow)$ is not yet clear. There seem to be two possibilities: (i) There are domains with M-point distortions, which increasingly suppress domains which are in the incommensurate state, when the temperature is decreased from 482.5 °C; and (ii) a superposition of a modulation of the chain occupation with a commensurate $\vec{q} = \vec{q}_M$ and an incommensurate $\vec{q} = \vec{q}_M \pm \vec{q}_\delta$ [Fig. 6(b)].

$$n(\uparrow) = n(\uparrow)_0 \mathrm{Re}\,\eta_M(T)[1 + \eta_\delta(T) e^{\pm i \vec{q}_\delta \cdot \vec{R}_l}] e^{i \vec{q}_M \cdot \vec{R}_l} .$$

Here $\vec{R}_l$ denotes the position of a Li^+ ion in the lth unit cell of the high-temperature phase, $n(\uparrow)_0 \cong \frac{3}{4}$ is the average spin up (or chain type 1) occupation, $n(\downarrow) = 1 - n(\uparrow)$; $\eta_M(T)$ and $\eta_\delta(T)$ denote the amplitudes of the commensurate and incommensurate distortions, respectively [Fig. 6(b)]. Also for this latter case, a Landau theory should be able to explain the suppression of $\eta_\delta(T)$ with growing $\eta_M(T)$.

Further work, both experimental and theoretical is in progress.

ACKNOWLEDGMENTS

The authors would like to thank J. Axe, H. Grimm, A. Hüller, D. Landau, and H. Stiller for many illuminating discussions and H. Spitzer for his help with the experiment.

---

[1] H. Böhm, Phys. Status Solidi A 30, 581 (1975).

[2] U. v. Alpen, H. Schulz, G. H. Talat, and H. Böhm, Solid State Commun. 23, 911 (1977).

[3] H. G. F. Winkler, Acta Crystallogr. 1, 27 (1948).

[4] V. Tscherry, H. Schulz, and F. Laves, Z. Kristallogr. 135, 175 (1972).

[5] V. Tscherry and F. Laves, Naturwissenschaften 57, 194 (1970).

[6] W. W. Pillars and D. R. Peacor, Am. Mineralog. 58, 681 (1973).

[7] H. Schulz and V. Tscherry, Acta Crystallogr. Sec. B 28, 2168 (1972).

[8] H. Schulz and V. Tscherry, Acta Crystallogr. Sec. B 28, 2174 (1972).

[9] H. Guth and G. Heger, Eleventh International Congress of Crystallogr., Warsaw, Poland, 1978 (unpublished); Proceedings of the International Conference on Fast Ion Transport in Solids, Lake Geneva, Wisconsin, USA, 1975 (unpublished), p. 499.

[10] The precise value seems to depend on details of the technique applied for the crystal growth and may be related to stoichiometry.

[11] H. D. Megaw, *Studies in Physics and Chemistry* (Saunders, Philadelphia, 1973), Vol. 10, p. 453.

[12] H. Grimm and B. Dorner, J. Phys. Chem. Solids 36, 407 (1975).

[13] J. Neubüser and H. Wondratschek, Kristall. Technik. 4, 529 (1966).

[14] E. Schönherr and E. Schedler, J. Cryst. Growth 42, 289 (1977).

[15] H. Glättli, G. L. Bacchella, M. Fourmond, A. Malinovski, P. Mériel, M. Pinot, P. Roubeau, and A. Abragam, J. Phys. (Paris) (to be published).

[16] G. E. Bacon, *Neutron Diffraction* (Clarendon, Oxford, 1975).

[17] T. Springer, *Springer Tracts in Modern Physics* (Springer, Berlin, 1972), Vol. 64.

[18] G. Eckold, K. Funke, J. Kalus, and R. E. Lechner, J. Phys. Chem. Solids 37, 1097 (1976).

[19] N. Wakabayoshi, S. M. Shapiro, and J. Axe (unpublished).

[20] J. D. Axe, Proceedings of the Conference on Neutron Scattering, Oak Ridge National Laboratory, Tennessee, 1976 (unpublished).

[21] W. L. McMillan, Phys. Rev. B 14, 1496 (1976).

[22] C. J. de Pater, J. D. Axe, and R. Currat (unpublished).

[23] H. Böhm and W. Hoffmann, Ferroelectrics 19, 19 (1978).

[24] H. Böhm, Z. Kristallogr. 148, 207 (1978).

[25] J. M. Hastings, J. P. Ponget, G. Shirane, A. J. Helger, N. D. Miro, and A. G. McDiarmid, Phys. Rev. Lett. 39, 1484 (1977).

[26] V. J. Emery and J. D. Axe, Phys. Rev. Lett. 40, 1507 (1978).

[27] O. V. Kovalev, *Irreducible Representations of the Space Groups* (Gordon and Breach, New York, 1965).

[28] B. D. Metcalf, Phys. Lett. A 46, 325 (1974).

[29] D. P. Landau and J. Ledford, Bull. Am. Phys. Soc. 23, 17 (1978).

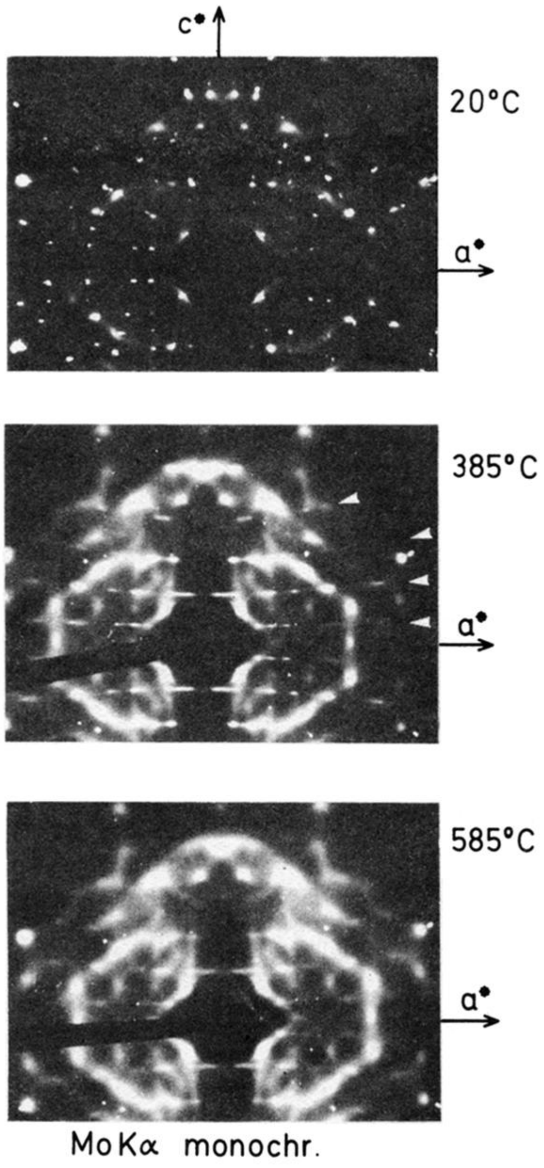

FIG. 2. Photographs taken with fixed film, fixed crystal, and monochromatic Mo $K\alpha$ radiation. Orientation of the crystal and investigation temperature are marked in the figure. The diffuse intensities at 385 and 585 °C in the form of very broad lines are caused by thermal diffuse scattering. The diffuse intensities in form of narrow lines parallel to a at $l=1,3,5,7$ (marked by white arrows at the 385 °C photograph) are caused by the one-dimensional ordering of the lithium ions in the structural main channels. These lines are generated by the so called a reflections (see text), which become more and more diffuse perpendicular to the c axis, e.g., the three-dimensional ordering is reduced more and more. These lines become broader also parallel to c at 585 °C. From the broadness parallel to c follows a correlation length of approximately 10 Li-Li distances per ordered chain.