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1992 J. Phys.: Condens. Matter 4 4399

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The incommensurate phase of sodium carbonate: an infrared absorption study

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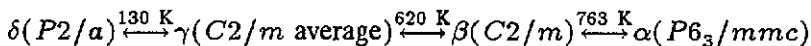
Received 1 October 1991, in final form 30 January 1992

Abstract. The α - β , β - γ and γ - δ transitions in Na_2CO_3 are observed through frequency changes in the carbonate ion internal modes. The incommensurate phase shows particularly interesting behaviour, as the ν_4 mode splits into two components at the β - γ transition which represent edge singularities. As the temperature is lowered five other, weaker components appear as subsidiaries to the edge singularities. These are interpreted as representing commensurate domains in a multisoliton lattice. It is shown that by solving the sine-Gordon equation numerically it is possible to calculate theoretical lineshapes in good agreement with the experimental spectra, although at the moment this must necessarily be done using a physically unrealistic model.

1. Introduction

The γ phase of Na_2CO_3 is the only known incommensurate phase among the alkali carbonates, and is remarkably similar in behaviour to the A_2BX_4 systems such as Rb_2ZnCl_4 and Rb_2ZnBr_4 , which have been studied extensively by Blinc and coworkers (Blinc *et al* 1986), chiefly using NMR spectroscopic techniques. The approach developed by Blinc for the interpretation of NMR spectra has been applied here to the infrared spectrum of Na_2CO_3 , which shows evidence for the existence of a multisoliton lattice, which is similar to that observed using NMR in Rb_2ZnCl_4 and Rb_2ZnBr_4 .

At atmospheric pressure Na_2CO_3 exists as four polymorphs (called α , β , γ , and δ with decreasing temperature), with continuous phase transitions between the α , β , and γ phases. The α phase has hexagonal symmetry ($P6_3/mmc$), hence it follows from the continuity of the transitions that the β and γ phases must be pseudo-hexagonal. A characteristic structural feature of α - Na_2CO_3 is that half of the Na^+ ions sit at the centres of NaO_6 octahedra, which share faces with each other so as to form infinite one-dimensional strings of octahedra parallel to the c axis.



De Wolff and Tuinstra (1986) suggested that the octahedral strings can be envisaged as part of a flexible backbone with the carbonate groups between them acting as

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fairly rigid hinges. The β phase is then simply the result of a σ_5 homogeneous shear strain, where the strings are sheared against each other with only a small amount of distortion in the actual shape of the NaO_6 octahedra and carbonate groups. The γ phase may then be thought of as consisting of a periodic bending back and forth of the strings, with the intermediate carbonate groups still acting as freely hinging connections. The modulation is one-dimensional with the incommensurate wavevector, q , roughly parallel to the space-averaged normal of the carbonate groups and close to the reciprocal lattice vector $[1, 0, 2]$, with a lock-in at

$$q_0 = \frac{1}{6}a^* + \frac{1}{3}c^*.$$

One important feature of $\gamma\text{-Na}_2\text{CO}_3$ is that it has a relatively large amplitude of modulation. A structure refinement of the γ phase by van Aalst *et al* (1976), assuming an harmonic modulation, found that the modulation is polarized along the b axis for most of the atoms, with amplitudes of up to 0.4 Å at room temperature, and that only two oxygen atoms of every carbonate group have polarization components along a and c as well. The result is a displacive modulation along the b axis combined with a libration of the carbonate groups in their plane and around the C-O bond perpendicular to b . The carbonate groups themselves are comparatively unperturbed, with a planarity of better than 0.002 Å and C-O and O-O bonds typical of most other carbonates (1.28–1.29 Å and 2.22 Å, respectively (van Aalst *et al* 1976)). At room temperature the waveform is already distorted relative to a purely sinusoidal waveform (Hogervorst *et al* 1979) and the modulation wavelength is approximately 16.3 Å (Dubbeldam and de Wolff 1969). The incommensurate wavevector locks in to a commensurate value at 130 K, resulting in the δ phase which has a commensurate $P2/a$ unit cell (de Pater and Helmholtz 1979). This represents a 12-fold increase in volume with respect to the β -phase unit cell.

The mid-infrared spectrum of anhydrous Na_2CO_3 was measured by Buijs and Schutte (1961), who assigned the observed peaks to the ν_1 , ν_2 , ν_3 and ν_4 vibrations of the carbonate ion, but could do little more, as the room-temperature structure was then not known.

Brooker and Bates (1971) performed more comprehensive Raman and infrared spectroscopic investigations of Na_2CO_3 at 300 K and 80 K, and observed the development of the all-important doublet structure of ν_4 which is investigated here in some detail. Maciel and Ryan (1981a, b) measured the Raman spectrum as a function of temperature and in particular the splitting of the ν_1 mode, which they found to be proportional to temperature. In both of these papers the splitting was explained as being due to a two-site effect, although the carbonate sites in question must actually be crystallographically equivalent as the modulation in the γ phase has a glide plane as a symmetry element (van Aalst *et al* 1976, de Wolff and Tuinstra 1986). As a possible alternative, Maciel and Ryan (1981b) offered the more likely explanation that the doublet structure is actually due to edge singularities in the frequency distribution function for the carbonate groups, as shown for the NMR spectra of several other incommensurate phases by Blicn (1981).

An important study was published by Meekes *et al* (1986), who measured the Raman and far-infrared spectra of all four phases of Na_2CO_3 very carefully. They observed two soft modes, one corresponding to the α - β transition and the other to the β - γ transition, and also confirmed the existence of the lock-in transition at 130 K, which had previously been observed in a neutron scattering experiment (de

Pater and Helmholtz 1979). More importantly, they showed that the Blinc model (Blinc 1981, de Wolff and Tuinstra 1986) could be used to interpret the Raman and infrared spectra of $\gamma\text{-Na}_2\text{CO}_3$ in order to qualitatively ascertain the shape of the modulation waveform as it varies with temperature.

In order to determine the characteristics of the three phase transitions and the incommensurate waveform in more detail, the fine structure of the infrared absorption signals from the internal modes of the molecular carbonate ion were investigated in this study. The ν_4 mode proved to be particularly sensitive, and, although it is not yet understood how to fully incorporate the infrared absorption matrix element, its lineshape was fitted with some success using the Blinc model.

2. Experimental details and results

The Na_2CO_3 sample used was obtained commercially as a powder and was kept in a drying oven at 120°C to ensure that it was always totally anhydrous. All measurements were made using pellets with a KBr diluent, except for those where the temperature dependence of the ν_2 vibration was investigated, where CsI was used in an attempt to reach higher temperatures before sintering of the matrix occurred.

Each spectrum was measured with a resolution of 1 cm^{-1} by 512 scans in the mid-infrared range ($2000\text{--}400\text{ cm}^{-1}$) using a Bruker 113v Fourier transform infrared spectrometer. The sample temperature was controlled using a Leybold liquid helium refrigeration cryostat (below room temperature) and a cylindrical platinum wound furnace with a Eurotherm temperature control system (for room temperature and above).

Spectral calculation was performed using boxcar apodization, as this allowed for optimum resolution of the overlapping bands in the ν_4 region in order to obtain the natural linewidth. The resultant side-lobes (often produced as a consequence of this type of apodization) were almost negligible in this case, and consequently no spectral smoothing of any sort was required.

The room temperature mid-infrared spectrum of $\gamma\text{-Na}_2\text{CO}_3$ is shown in figure 1 and shows all of the expected infrared-active internal modes. The ν_2 vibration (out-of-plane bend) is clearly split into two bands; one very intense and the other comparatively weak. The temperature dependence of the main peak was measured above room temperature; the frequency change, though quite small, clearly shows the two high-temperature transitions, $\alpha\text{--}\beta$ and $\beta\text{--}\gamma$ (figure 2).

The ν_4 mode (in-plane bend) is present as a single band in the high temperature (α) phase, and eventually splits into seven components at lower temperatures (in the δ phase), (figures 3 and 4). This behaviour is entirely as expected from symmetry considerations (Meekes *et al* 1986). The ν_4 mode has E' symmetry in the free carbonate ion, which reduces to E_{1u} in the α phase and $A_u + B_u$ in the β phase (accounting for only the relevant infrared-active vibrations). On cooling, the $\alpha\text{--}\beta$ transition is observed through the appearance of a weak additional peak in the β phase, which is first seen at 730 K at about 694 cm^{-1} . This peak is assigned to the B_u representation, as the modulation has displacements parallel to the b axis and the splitting of the two most intense peaks in the γ phase should then be strongest for the A_u representation rather than B_u (Meekes *et al* 1986). The strong component which splits at the $\beta\text{--}\gamma$ transition must therefore be the A_u mode. The B_u component is so low in intensity that it is only observable as a slight shoulder to the A_u peak in the β

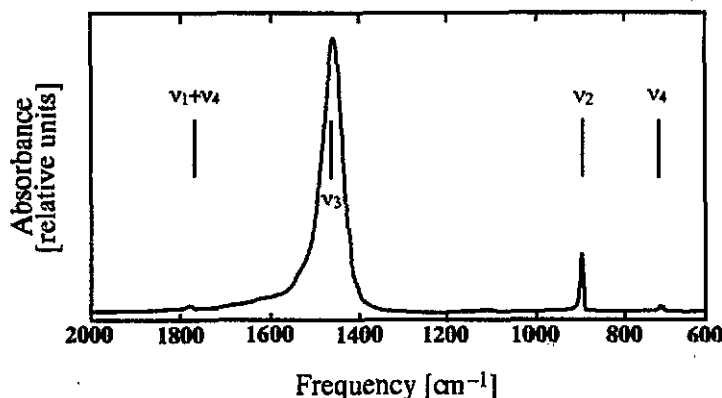


Figure 1. The room-temperature spectrum of the infrared-active internal modes of Na_2CO_3 .

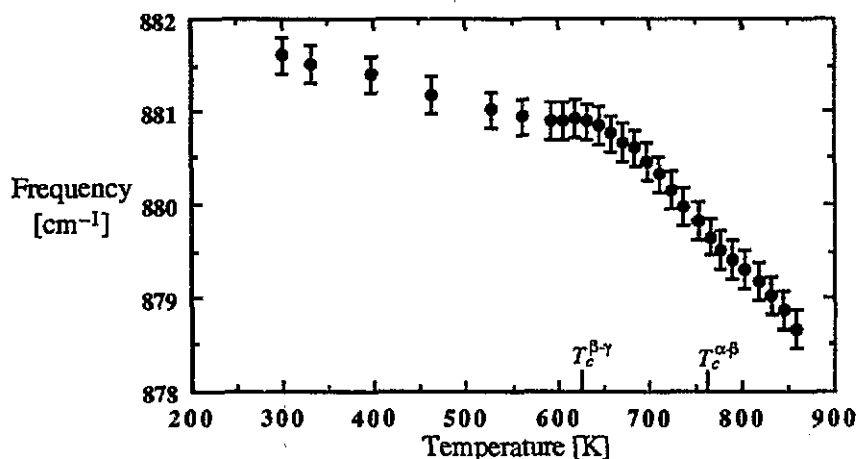


Figure 2. The temperature dependence of the strongest component of ν_2 .

phase, and cannot be distinguished at all in the γ phase. It is therefore assumed that all ν_4 peaks observed in the γ phase correspond to the A_u representation. In the γ phase, the A_u component first splits into two main components, with other weaker bands appearing as the temperature is lowered further. These two main bands move closer together in frequency as the temperature is raised, until they merge at the β - γ transition, in a manner similar to that observed for ν_1 by Maciel and Ryan (1981a, b). The lock-in transition is characterized by the appearance of two small side-bands at 709 cm^{-1} and 692 cm^{-1} , making a total of seven observed peaks, following the sequence:

$$E_{1u}(\alpha) \rightarrow A_u(\beta) \rightarrow (\gamma) \rightarrow 4A_u + 3B_u(\delta).$$

This does, of course, ignore the B_u peak in the β phase, which would also split into seven components if it were observed.

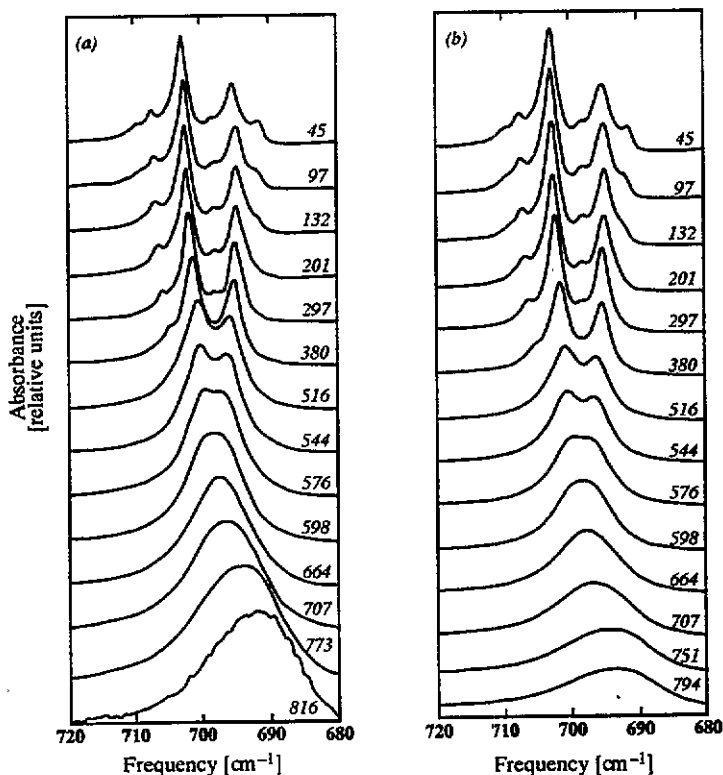


Figure 3. The ν_4 mode at various temperatures (in K), with (a) the absorbance scale normalized for each spectrum to show detail, and (b) true to scale.

3. Discussion

The frequencies of the carbonate ion internal modes are all fairly high (greater than 700 cm^{-1}) due to the strong C-O bonds, hence the coupling of the internal modes to the lattice, and therefore the dispersion of the modes, is relatively small. In fact their frequencies are only slightly shifted from the values for the free carbonate ion (approximately 7 cm^{-1} for ν_4). It is therefore assumed that the internal modes may be treated as local modes, with the frequencies being determined by the local symmetry of the carbonate ion.

In different parts of the crystal, the field acting on each carbonate ion due to the modulation takes all values between zero and the value corresponding to maximum displacement. Following the arguments of Blinc *et al* (1986) for a one-dimensional modulation along the x axis, the frequency, ω_i , of the i th internal mode must therefore be written as a function of the displacement $u(x)$,

$$\omega_i = \omega(u(x)) \quad (3.1)$$

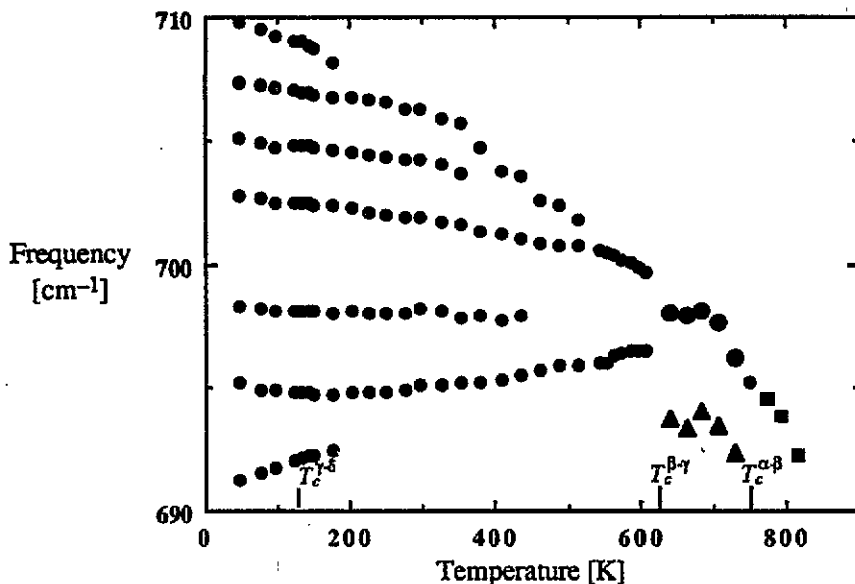


Figure 4. The temperature evolution of the absorption frequencies of the ν_4 mode over the entire temperature range studied. The error on each data point is indicated by its size. A_u component = circles, B_u = triangles, E_{1u} = squares.

which can be expanded in powers of $u(x)$, as was also suggested by Meekes *et al* (1986),

$$\omega_i = \omega_i^0 + a_{i1}u(x) + \frac{1}{2}a_{i2}u^2(x) + \dots \quad (3.2)$$

where a_{ij} are constants. Writing u as $u = A \cos \phi(x)$ (where the amplitude has a temperature dependence $A = [(T_c^{\beta-\gamma} - T)/T_c^{\beta-\gamma}]^\beta$, β is the critical exponent and $\phi(x)$ is the phase of the modulation), equation (3.2) becomes

$$\omega_i = \omega_i^0 + \omega_{i1} \cos \phi(x) + \frac{1}{2}\omega_{i2} \cos^2 \phi(x) + \dots \quad (3.3)$$

In a more general case, where non-local contributions are accounted for (i.e. mode coupling of adjacent carbonate ions), the real displacement u is given by an admixture of symmetric and antisymmetric components (Blinic *et al* 1985)

$$u = u_0^s \cos \phi(x) + u_0^a \sin \phi(x). \quad (3.4)$$

Dropping the suffix i (as only the ν_4 mode is considered here), (3.3) can eventually be rearranged to give

$$\omega(x) = \omega_0 + \omega_1 \cos[\psi(x) + \Phi] + \omega_2 + \omega_2' \cos^2 \psi(x) + \dots \quad (3.5)$$

where $\psi(x)$ and Φ are renormalized phase angles (Blinic *et al* 1985).

Assuming that the modulation is constant in amplitude over the entire volume of the crystal, the infrared frequency distribution function is

$$f(\omega) \propto \left(\frac{\partial \omega}{\partial x} \right)^{-1} = \left(\frac{\partial \omega}{\partial \psi} \frac{\partial \psi}{\partial x} \right)^{-1} \quad (3.6)$$

and the actual lineshape is determined by the convolution of $f(\omega)$ with the lineshape function $L(\omega - \omega_c)$

$$F(\omega) = \int_0^{\infty} L(\omega - \omega_c) f(\omega_c) d\omega_c. \quad (3.7)$$

From (3.6), singularities appear in the spectrum when $\partial\omega/\partial\psi$ and/or $\partial\psi/\partial x$ tend to zero. In the 'plane-wave' limit when the modulation waveform is purely sinusoidal, $\partial\psi/\partial x$ is constant and the only singularities present are those associated with $\partial\omega/\partial\psi$, which are called the 'edge singularities'. This can be seen in the ν_4 spectra for Na_2CO_3 (figures 3 and 4): between 620 K and about 520 K only two peaks can be resolved—these are the edge singularities. Below 520 K additional peaks appear and eventually the full complement of seven peaks for the lock-in phase is observed below and actually above the lock-in transition (figure 4). The observation that in the incommensurate phase there are more peaks present than just the two edge singularities suggests that the modulation waveform is no longer simply sinusoidal (as was observed in a structure refinement at room temperature by Hogervorst *et al* 1979) and that commensurate regions exist in the crystal.

McMillan (1976) originally suggested the concept of phase solitons, or 'discommensurations', to explain the observation of high-order harmonics in the incommensurate modulation waves from certain systems. These harmonics tend to appear as the temperature is lowered closer to the lock-in temperature, producing a 'squaring-up' effect of the originally purely sinusoidal waveform. When this happens, the incommensurate phase is then best described as consisting of commensurate regions where the phase is constant, separated by domain walls, or phase solitons, where the phase changes rapidly. This distortion of the phase minimizes the Landau free energy of the system, and the resulting non-linear differential equation is known as the sine-Gordon equation. Therefore, it is suggested here that the appearance of extra peaks to the edge singularities in the ν_4 spectrum is due to the existence of this so-called multisoliton lattice, as has been observed in several other incommensurates using techniques such as NMR (Blinic *et al* 1986) and NQR (Aleksandrova 1986).

In general then, $\partial\psi/\partial x$ is not constant (especially as the lock-in transition is approached) and the phase ψ will be constant in the commensurate domains where $\partial\psi/\partial x$ tends to zero, but will change rapidly with x in the solitonic domain walls, where $\partial\psi/\partial x \neq 0$. The appearance of commensurate domains will thus result in the appearance of commensurate lines in the spectrum and a reduction in the intensity of the edge singularities.

From equation (3.6) it is possible to calculate the infrared lineshape for different temperatures. The differential $\partial\omega/\partial\psi$ can be found by differentiating (3.5), and $\partial\psi/\partial x$ is given by integrating the sine-Gordon equation (Blinic *et al* 1986),

$$\partial\psi/\partial x \propto [\Delta^2 + \cos^2\{n(\psi - \phi_0)/2\}]^{1/2} \quad (3.8)$$

where $\psi(x) = \phi(x) + \phi_0$, Δ is the integration constant, n is the order of anharmonicity for the Umklapp energy which drives the lock-in transition—for Na_2CO_3 , $n = 12$ (de Pater and Helmholtz 1979)—and ϕ_0 is the initial phase angle which depends on the offset between the modulation wave and the origin of the high-temperature commensurate unit cell.

In practice, Δ is varied to fit (3.6) to the experimental lineshape at each temperature, and the density of phase solitons may then be calculated from the value of Δ .

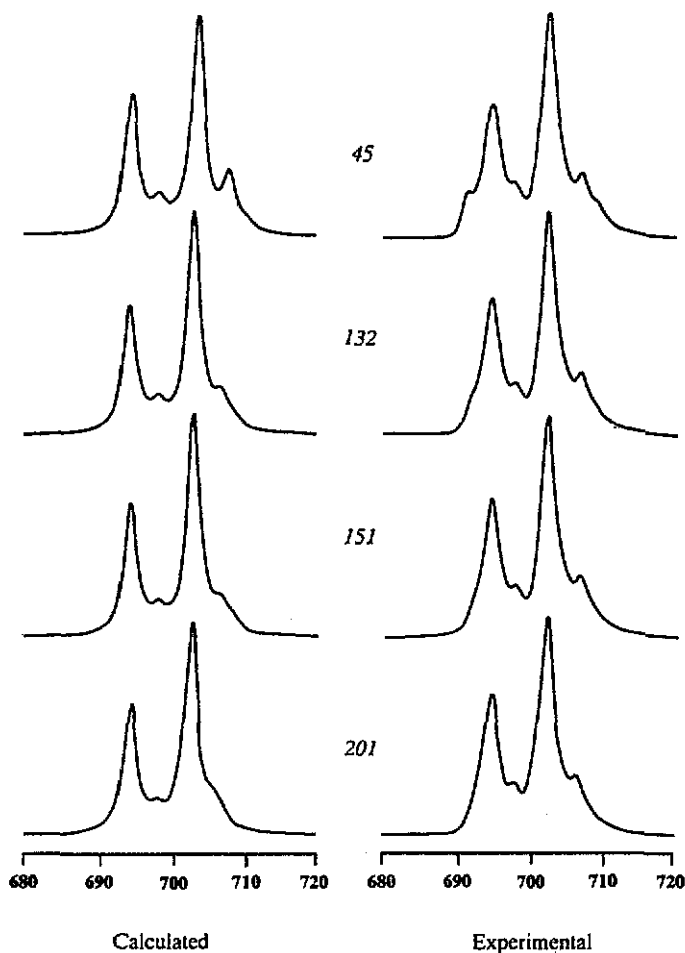


Figure 5. Comparison between the calculated and experimental lineshapes for the ν_4 mode in Na_2CO_3 close to the lock-in transition. (Temperatures in K.)

The temperature dependence of the soliton density in an incommensurate phase is of considerable interest (Blinic *et al* 1986).

Unfortunately, this model does not include the matrix element for the infrared absorption process, and it is actually not known at present how to incorporate it. Hence, the model is expected only to describe infrared experimental results rather approximately at best. This difficulty is particularly acute in the case of the ν_4 mode of Na_2CO_3 , as the infrared absorption selection rules mean that out of the twelve components in the lock-in phase, only seven are actually infrared active (Meekes *et al* 1986) i.e. a calculation of the ν_4 lineshape with the correct value of $n = 12$ gives the inappropriate number of twelve peaks. It is possible to adjust the calculation to give the observed number of seven peaks by varying ϕ_0 , but this only makes some of the components degenerate and does not actually remove them completely, as is necessary. An attempt was made to calculate the ν_4 lineshape using $n = 12$, but it was not possible to attain any agreement with the observed spectra for the above

reason. Another alternative, although physically rather unjustifiable as it results in the wrong lock-in energy, is to calculate the lineshape with the value of $n = 7$. This was also attempted in this study with a greater degree of success by using the expansion

$$\omega = \omega_0 + \omega_{1a}\alpha^\beta \cos(\psi(x) + \Phi) + \omega_{2a}\alpha^{2\beta} + \omega_{2b}\alpha^{2\beta} \cos^2 \psi(x) + \omega_{3a}\alpha^{3\beta} \\ \times \cos^3 \psi(x) + \omega_{4a}\alpha^{4\beta} \cos^4 \psi(x) \quad (3.9)$$

$$\alpha = (T_c^{\beta-\gamma} - T) / T_c^{\beta-\gamma}$$

with the following temperature-independent coefficients, which were obtained by fitting to the positions of the edge singularities at different temperatures: $\omega_0 = 698.0 \text{ cm}^{-1}$, $\omega_{1a} = 2.9 \text{ cm}^{-1}$, $\omega_{2a} = 5.6 \text{ cm}^{-1}$, $\omega_{2b} = -7.5 \text{ cm}^{-1}$, $\omega_{3a} = 6.1 \text{ cm}^{-1}$, $\omega_{4a} = 7.4 \text{ cm}^{-1}$ and $\Phi = 0.0^\circ$.

The critical exponent β was chosen to be equal to 0.36 for the expansion in the γ and δ phases. This was the value found by Maciel and Ryan (1981a), in common with the value of β for several other incommensurate phases such as Rb_2ZnCl_4 and Rb_2ZnBr_4 (Blinic *et al* 1986). ϕ_0 was chosen to give the observed positions of the commensurate peaks ($\phi_0 = 206.0^\circ$).

These coefficients gave a good agreement with the observed spectra close to the lock-in temperature and up to about 300 K (figure 5), but above this temperature they failed to reproduce the relative intensities of the edge singularities accurately. Even so, the actual positions of all calculated peaks were accurate to within $\pm 0.3 \text{ cm}^{-1}$ of the observed values, and the intensities of the commensurate peaks could still be fitted adequately above this temperature.

The actual value of n only determines the number of calculated peaks in the model and does not actively control the positions and intensities of the commensurate peaks relative to the edge singularities; this is the reason why a good agreement has been observed between the calculated spectra (with a physically incorrect value for n) and the experimentally observed spectra. It is necessary to develop a model which includes the infrared absorption matrix element to fully interpret the experimental results presented in this paper and to calculate the soliton density satisfactorily.

Acknowledgments

The authors would like to thank Professor R A Cowley for helpful discussions and advice. MJH acknowledges the receipt of an NERC studentship.

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