

interpreted as a mixed phase and its spectrum as the superposition of the spectra of two other phases, III and IV. The spectrum of phase V contains modes ( $\nu_5(\text{TO})$ ) and ( $\nu_5(\text{LO})$ ) that correspond to each fundamental mode of phase IV, and, in addition, five lattice phonons ( $\nu_7''$ ,  $\nu_7'$ ,  $\nu_5''$ ,  $\nu_5'$ , and  $\nu_6'$ ) which correspond to the spectra of phase III. The superimposed spectra of the parallel ordered  $\text{NH}_4\text{Br}$  IV and the antiparallel ordered  $\text{NH}_4\text{Br}$  III are shown in fig. 4. A mixed phase can be expected in a pseudo-spin system as in  $\text{NH}_4\text{Br}$  where a parallel and an antiparallel oriented phase are already present; examples of mixed phases are well known in magnetic systems [12,13].

#### 4. Summary

Raman studies of the high pressure phase V of  $\text{NH}_4\text{Br}$  and  $\text{ND}_4\text{Br}$  are reported. Deuteration lowers the II-V phase transition pressure from 20 to 9 kbar at 296 K, which is certainly welcome since many more experimental techniques are available at lower pressures. The main features of the results for  $\text{NH}_4\text{Br}$  V, namely (1) the anomalous and strongly temperature-dependent intensity of the Raman peaks, and (2) the small volume-dependent anharmonicity, can be interpreted on the basis of a mixed phase. The two dynamic domains or clusters in phase V are identified as the parallel and antiparallel configurations that one observes in  $\text{NH}_4\text{Br}$  IV and III, respectively, while the new low energy shoulder ( $\nu_5''(\text{B}_{2g})$ ) appearing on  $\nu_5(\text{TO})$  at the II-V transition represents the translational motion of the  $\text{NH}_4^+$  ions in the *c* direction of the antiparallel configuration. The five lattice modes becoming Raman inactive at the V-IV transition can be assigned to clusters with antiparallel  $\text{NH}_4^+$  ions in  $\text{NH}_4\text{Br}$  V. The  $\text{NH}_4^+$  ion ordering is an essential feature of the II-V transition although the polarization

of the  $\text{Br}^-$  ion would be a very important factor in stabilizing the clusters with the antiparallel configuration [14].

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#### References

- [1] C.W. Garland and R.A. Young, *J. Chem. Phys.* 49 (1968) 5282.
- [2] Y. Ebisuzaki, *Chem. Phys. Letters* 19 (1973) 503; *J. Chem. Phys.* 61 (1974) 3170; to be published.
- [3] W.G. Fateley, F.R. Dollish, N.T. McDevitt and F.F. Bentley, *Infrared and Raman selection rules for molecular and lattice vibrations* (Wiley, New York, 1972).
- [4] R.B. Wright and C.H. Wang, *J. Phys. Chem. Solids* 34 (1973) 787.
- [5] C.H. Perry and R.P. Lowndes, *J. Chem. Phys.* 51 (1969) 3648.
- [6] Y. Ebisuzaki, *J. Crystal Growth* 26 (1974) 301.
- [7] V. Hovi, in: *Proc. Intern. Conf. Sci. Tech. Non-Metallic Crystals*, New Delhi, India (1969) p. 67.
- [8] R. Stevenson, *J. Chem. Phys.* 34 (1961) 1757.
- [9] K.B. Harvey and N.R. McQuaker, *J. Chem. Phys.* 55 (1971) 4390.
- [10] Y. Yamada, Y. Noda, J.D. Axe and G. Shirane, *Phys. Rev. B* 9 (1974) 4429.
- [11] C.H. Wang and R.B. Wright, *J. Chem. Phys.* 61 (1974) 339.
- [12] R.J. Birgeneau, G. Shirane, M. Blume and W.C. Koehler, *Phys. Rev. Letters* 33 (1974) 1098.
- [13] J.A. Griffin, S.E. Schnatterly, Y. Farge, M. Regis and M.P. Fontana, *Phys. Rev. B* 10 (1974) 1960.
- [14] T. Nagamiya, *Proc. Phys. Math. Soc. Japan* 25 (1943) 540; *J. Chem. Phys. Suppl.* 49 (1952) 251.