69, 2101 (1965).

[6] T. E. Haas and E. P. Marram, J. Chem. Phys. 43, 3985 (1965).

[7] R. L. Armstrong, G. L. Baker, and K. R. Jeffrey, Phys. Rev. B 1, 2847 (1970).

[8] G. L. Baker and R. L. Armstrong, Can. J. Phys. 48, 1649 (1970).

[9] R. L. Armstrong and G. L. Baker, Can. J. Phys. 48, 2411 (1970).

[10] E. Pytte and J. Feder, Phys. Rev. 187, 1077 (1969).

PHYSICAL REVIEW B VOLUME 3, NUMBER 9 1 MAY 1971

Comment on the Pressure Dependence of the ^{35}Cl Nuclear Quadrupole Resonance in K_2ReCl_6

G. P. O'Leary
Oregon Graduate Center for Study and Research, Portland, Oregon 97225

(Received 4 November 1970)

Our previous comments[1,2] regarding the interpretation of nuclear-quadrupole-resonance (NQR) spectra were inspired mainly by the simple observation that a Bose-Einstein–like temperature dependence is not very sensitive to the details of the mechanisms responsible for it. Alternatively stated, thermodynamic data alone are generally insufficient to prove or disprove a microscopic model.

Thus, for the case in point of the ^{35}Cl resonance in the K_2MCl_6 series of salts, we have argued that one must bring the results of other experiments to bear on the problem before hard and fast conclusions can be drawn. To this end, we introduced x-ray and spectroscopic data and the results of a lattice-dynamics calculation done for K_2ReCl_6. At the time we were able to make an admittedly limited, but internally consistent description of *all* the data available to us in terms of the soft-mode model for the 110 °K phase transition of K_2ReCl_6.

Since that time we have noted with pleasure that others have followed our suggestion and started to incorporate spectroscopic data into their NQR temperature-dependence discussions.[3,4] We were equally happy to see the appearance of the preceding paper[5] which presents the preliminary results of a systematic study of the NQR pressure dependence in these salts.

The "raison d'etre" for our making a comment here is that we feel that our earlier observation is still valid. Namely, validation of a microscopic model requires more than thermodynamic data.

Firstly, let us point out several pieces of existing data that point to the fact that the π-bonding scheme alone is insufficient to provide a consistent interpretation.

On the purely thermodynamic level, information has been available for some time on the thermal expansion of the R_2MX_6 salts. The volume expansion coefficient α for K_2SnBr_6 was found by Galloni *et al.*[6] to be 155×10^{-6} °K^{-1}. Their x-ray data are quite interesting in that they show that the volume varies linearly with temperature just above the phase transition. If K_2ReCl_6 behaves similarly, as we expect it to, there will be no nonlinearities in the NQR spectra above 110 °K due to volume effects. Our own x-ray data on K_2ReCl_6 (see Fig. 5 of Ref. 2) indicate that between 110 and 300 °K the average value of α is $\sim 125 \times 10^{-6}$ °K^{-1}, thus partially confirming the similarity.

Compressibilities are also fairly well known. The lattice dynamics calculation of Ref. 2 yields a longitudinal sound velocity of $\sim 3.4 \times 10^5$ cm/sec and a transverse sound velocity of $\sim 1.3 \times 10^5$ cm/sec. Combining these velocities with the known density[7] of 3.325 g/cm^3 gives a compressibility β of 3.2×10^{-6} cm^2 kg^{-1}. Thus, the thermodynamic parameter α/β in fact has a value of ~ 40 kg cm^{-2} °K^{-1} which is nearly an order of magnitude larger than that used in the preceding paper.[5] This implies that the $(\partial\nu/\partial T)_P = (\partial\nu/\partial T)_V$ assumption is invalid for the entire series of salts. In addition, substitution of this value of α/β into Eq. (2) of the preceding paper,[5] using the values of the other parameters as stated there, implies that the product $n\xi$, the π-bonding parameter, is nearly zero.

Molecular-orbital calculations have been performed for the MCl_6 (M = Pt, Ir, Os, Re) radical by Cotton and Harris.[8] These calculations indicate that the hole in the chlorine $3p_\pi$ orbitals is about 0.05*e* for Ir, Os, and Re. The fact that the calculated π occupation does not vary significantly would seem to argue that it is not an important parameter in the description of the systematics of the series of compounds. These calculations were based on spectroscopic data and in fact gave a very good fit to the observed NQR coupling constants.

One further remark is in order. The preceding authors have concentrated almost exclusively on the regions in which the NQR temperature and pressure dependence is linear to the exclusion of the rather intriguing regions where it is not. It has been and still is our contention that the real clue to the microscopic description of the NQR coupling constants lies in the nonlinear regions. To paraphrase the preceding authors concluding statement: A correct quantitative analysis must await the measurement of further effects.

---

[1] G. P. O'Leary, Phys. Rev. Letters 23, 782 (1969).

[2] G. P. O'Leary, and R. G. Wheeler, Phys. Rev. B 1, 4409 (1970).

[3] R. L. Armstrong, G. L. Baker, and K. R. Jeffrey, Phys. Rev. B 1, 2847 (1970).

[4] G. L. Baker and R. L. Armstrong, Can. J. Phys. 48, 1649 (1970).

[5] R. L. Armstrong, G. L. Baker, and H. M. Van Driel, preceding paper, Phys. Rev. B 3, 3072 (1971).

[6] E. E. Galloni, M. R. deBenycar, and M. J. deAbeledo, Z. Krist. 117, 470 (1962).

[7] H. E. Swanson, M. C. Morris, R. P. Strinchfield, and E. M. Evans, *Standard X-Ray Diffraction Powder Patterns*, Natl. Bur. Std. (U.S.) Monograph No. 25 (U.S. GPO, Washington, D. C., 1963), Sec. 2, p. 28.

[8] F. A. Cotton and C. B. Harris, Inorg. Chem. 6, 376 (1967).

PHYSICAL REVIEW B VOLUME 3, NUMBER 9 1 MAY 1971

ERRATA

Pair Distribution Function for Various Dielectric Functions, P. R. Antoniewicz and Leonard Kleinman [Phys. Rev. B 2, 2808 (1970)]. In Eq. (10), A should be replaced by B. The numerical calculations were performed with the correct formula.

Low-Temperature Elasticity and Magnetoelasticity of Dysprosium Single Crystals, M. Rosen and H. Klimker [Phys. Rev. B 1, 3748 (1970)]. The procedure of preparing figures for publication involved combining two or more computer plots on one figure. During this process the scale of C_{11} in Fig. 1 was erroneously decreased by 0.36 scale units. Thus the C_{11} scale should begin with the value of 6.92 instead of 6.56. The error has no effect whatever on either computer calculations or any other figures in the paper. A corrected version of the figure is shown to the right.

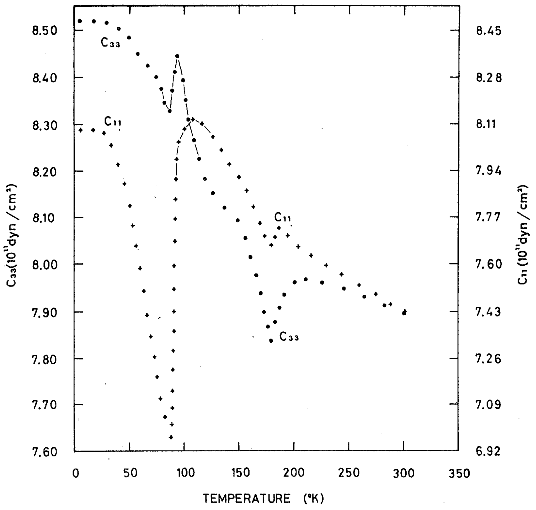

FIG. 1. Temperature dependence of the dilational elastic eoefficients C_{11} and C_{33} of dysprosium single crystals.