

COMMENTS AND ADDENDA

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Pressure Dependence of the ^{35}Cl Nuclear-Quadrupole-Resonance Frequency in K_2ReCl_6 †

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The temperature and pressure variation of the ^{35}Cl nuclear-quadrupole-resonance (NQR) frequency in K_2ReCl_6 is reported. The temperature variation is measured from 130 to 350 °K, and the pressure variation from 1 to 5000 kg cm⁻² at several temperatures between 275 and 350 °K. The data indicate that volume effects are extremely important. A simple model to describe the destruction of π bonding by the lattice vibrations is shown to provide a consistent description of the NQR-frequency data in K_2MCl_6 with $M \equiv \text{Pt}, \text{Ir}, \text{Os}, \text{and Re}$. The effect of the softening of the rotary lattice mode associated with the structural phase transition at 110.9 °K in K_2ReCl_6 is shown to be relatively small for temperatures between 275 and 350 °K.

INTRODUCTION

O'Leary^{1,2} has suggested that the temperature variation of pure nuclear-quadrupole-resonance (NQR) frequencies provides a practical means for the detection of soft librational modes in the spectrographically inaccessible regions. In particular, he has presented data for K_2ReCl_6 above its 110.9 °K phase transition. His analysis of these data indicates a marked temperature dependence of the frequency of the $\vec{k}=0$ rotary lattice mode. This result depends specifically on the assumption that the change of volume with temperature has a negligible effect on the NQR frequency. Because of the potential importance of O'Leary's suggestion, we decided to test the validity of this assumption by making measurements of the NQR frequency as a function of pressure at a constant temperature.

There was also a second reason for the present investigation. The electronic structures of the hexachloride complexes of the metals Pt, Ir, Os, Re, and W are very similar, with the exception that the number of electrons in the antibonding π^* orbital decreases by 1 as the series is descended.³ In K_2PtCl_6 , the π^* orbital is just filled and, from a consideration of the form of the molecular orbitals, it may be concluded that no net π delocalization of the halogen lone-pair electrons can occur. How-

ever, this effect should become apparent for K_2IrCl_6 and increase in a regular manner through K_2OsCl_6 , K_2ReCl_6 , and K_2WCl_6 . The series of compounds all have the same crystal structure in their high-temperature phase, with lattice constants and $M\text{-Cl}$ distances all equal to within 1.5%. It follows that the characteristic vibrational frequencies should be as nearly identical as one could expect from any series of compounds; this has been verified by infrared and Raman spectroscopic studies.⁴ The temperature dependence of the NQR frequency from non- π -bonding effects should be the temperature dependence as observed in K_2PtCl_6 . It has been suggested^{5,6} that the difference between the temperature dependence of the NQR frequency in K_2PtCl_6 and in other members of the series should be entirely due to the presence of π bonding. In a recent series of papers,⁷⁻⁹ we have adopted a simple model to describe the destruction of π bonding by the lattice vibrations and have obtained a self-consistent analysis of NQR frequency data in K_2PtCl_6 , K_2IrCl_6 , and K_2OsCl_6 . If our approach is a reasonable one then it should be possible to extend it to K_2ReCl_6 . O'Leary,¹ on the other hand, argues against π bonding as an explanation for the high-temperature positive derivative $(\partial\nu/\partial T)_p$ in K_2ReCl_6 . Some clarification concerning this difference of opinion is clearly required.

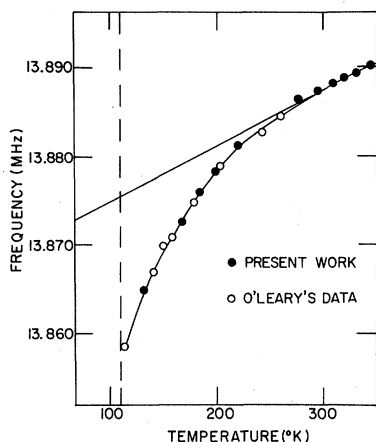


FIG. 1. Temperature variation of the ^{35}Cl NQR frequency in the high-temperature phase of K_2ReCl_6 . The straight line is tangent at 300°K to the curve drawn through the data.

EXPERIMENTAL DATA

A polycrystalline sample of K_2ReCl_6 , purchased from Johnson, Matthey, and Mallory, was used for the experiments. The experimental apparatus used and procedure adopted have been described in an earlier publication.⁸ Both the temperature and pressure variations of the ^{35}Cl resonance frequency were measured in the high-temperature phase.

The variation of the NQR frequency with temperature from the phase transition temperature $T_c = 110.9$ to 350°K is shown in Fig. 1. Both O'Leary's data¹ and the data obtained in the present experiments are shown. The two sets of data are compatible and are well represented by the smooth curve drawn through them. The straight line is the tangent to the curve drawn at 300°K . The slope of the line provides the value of $(\partial\nu/\partial T)_P$ at this temperature. It can be seen that $(\partial\nu/\partial T)_P$ is almost a constant for temperatures greater than 275°K . For temperatures below 275°K , $(\partial\nu/\partial T)_P$ increases with decreasing temperature. The extrapolation of the straight line in Fig. 1 to 0°K gives the static lattice resonance frequency $\nu_0 = 13.868$ MHz as it would be if the high-temperature phase extended to 0°K . Note that for his analysis, O'Leary used the value $\nu_0 = 14.050$ MHz obtained by the extrapolation of NQR data taken below the phase transition; this is a questionable step. The use of our extrapolated value for ν_0 leads to a breakdown of O'Leary's analysis.

In our previous studies^{8,9} of the ^{35}Cl resonance in K_2MCl_6 substances at temperatures greater than 350°K the response of the NQR frequency to changes in temperature was influenced by the onset of hindered rotational motions of the MCl_6 octahedra about their symmetry axes. A similar effect was

TABLE I. Summary of $(\partial\nu/\partial T)_P$ and $(\partial\nu/\partial P)_T$ values in K_2MCl_6 compounds.

Substance	$(\partial\nu/\partial T)_P$ (kHz $^\circ\text{K}^{-1}$)	$(\partial\nu/\partial P)_T$ (kHz $\text{kg}^{-1}\text{cm}^2$)
K_2PtCl_6	-0.933 ± 0.014	0.0050 ± 0.004
K_2IrCl_6	-0.570 ± 0.008	-0.0037 ± 0.003
K_2OsCl_6	-0.179 ± 0.008	-0.0071 ± 0.003
K_2ReCl_6	0.06 ± 0.01	-0.0112 ± 0.003

observed in the present studies which were extended to 450°K . The data obtained are not included in Fig. 1 since they are not relevant to the present discussion.

The variation of the ^{35}Cl NQR frequency with pressure was studied at a number of different temperatures between 275°K and 350°K . The data obtained at 277°K are presented in Fig. 2. The data indicate a linear decrease in frequency with increasing pressure over the range of pressures studied. The slope of the line provides the $(\partial\nu/\partial P)_T$ value at this temperature. This quantity was found to be essentially independent of temperature over the entire temperature range.

The $(\partial\nu/\partial T)_P$ and $(\partial\nu/\partial P)_T$ values for K_2PtCl_6 , K_2IrCl_6 , K_2OsCl_6 , and K_2ReCl_6 are summarized in Table I. Although strictly speaking, these partial derivatives are functions of both temperature and pressure, the experimental measurements suggest that over the range of temperatures $275 \leq T \leq 350^\circ\text{K}$ and the range of pressures $1 \leq P \leq 5000$ kg cm^{-2} they are very nearly constants.

DISCUSSION

The experimental quantities $(\partial\nu/\partial T)_P$ and $(\partial\nu/\partial P)_T$

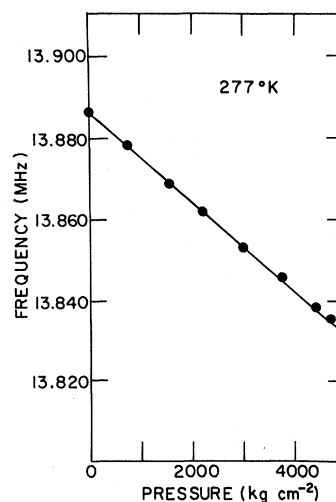


FIG. 2. Pressure variation of the ^{35}Cl NQR frequency in K_2ReCl_6 .

are related through the thermodynamic equation

$$\left(\frac{\partial\nu}{\partial T}\right)_P + \frac{\alpha}{\beta} \left(\frac{\partial\nu}{\partial P}\right)_T = \left(\frac{\partial\nu}{\partial T}\right)_V, \quad (1)$$

where α is the thermal expansion coefficient and β is the isothermal compressibility. Although experimental values of α and β do not exist for this K_2MCl_6 series of compounds the average ratio α/β has been estimated as $\sim 5 \text{ kg cm}^{-2} \text{ }^\circ\text{K}^{-1}$ from the simultaneous analysis of the NQR in K_2PtCl_6 , K_2IrCl_6 , and K_2OsCl_6 .⁹ It is to be noted that this estimate of α/β depends on the rather dubious assumption that the strength of π bonding is linear with the number of electrons in the antibonding π^* orbital. It is likely that α/β is, in fact, rather larger. From Table I, taking $\alpha/\beta = 5$, we see that the assumption $(\partial\nu/\partial T)_P = (\partial\nu/\partial T)_V$ is valid to within 5% for K_2PtCl_6 and K_2IrCl_6 , and to within 20% for K_2OsCl_6 . Clearly, the assumption is completely unrealistic for K_2ReCl_6 for which $|(\partial\nu/\partial T)_P| \approx |(\alpha/\beta)(\partial\nu/\partial P)_T|$.

This is the first result. Volume effects are important in K_2ReCl_6 . An analysis of NQR data having quantitative significance for temperatures close to the phase transition must await measurements of these effects.

Let us now see if the NQR results in the temperature range $275 \leq T \leq 350 \text{ }^\circ\text{K}$ are consistent with similar results for K_2PtCl_6 , K_2IrCl_6 , and K_2OsCl_6 . In a previous paper,⁹ we deduced the following expression for the partial derivative $(\partial\nu/\partial T)_V$:

$$\left(\frac{\partial\nu}{\partial T}\right)_V = \nu_0(M) \left(\frac{5\nu_{at}n\xi}{\nu_0(M)} - 3 \left(\frac{\partial\langle\theta^2\rangle}{\partial T} \Big|_V^{\text{int}} + \frac{\partial\langle\theta^2\rangle}{\partial T} \Big|_V^{\text{rot}} \right) \right). \quad (2)$$

In this equation, ν_{at} is the NQR frequency for a free chlorine atom in its ground state, $\nu_0(M)$ is the static lattice resonance frequency, ξ is a parameter which depends on the strength of the π bonding for a single t_{2g}^* hole, n is the number of t_{2g}^* holes, $\partial\langle\theta^2\rangle/\partial T|_V^{\text{int}}$ and $\partial\langle\theta^2\rangle/\partial T|_V^{\text{rot}}$ are the contributions to the mean square angular displacement of an M -Cl bond from equilibrium due to the internal modes and the rotary lattice mode, respectively. Our previous analysis gave the following average parameters for the three compounds: $\partial\langle\theta^2\rangle/\partial T|_V^{\text{int}} = 3.52 \times 10^{-6} \text{ rad}^2 \text{ }^\circ\text{K}^{-1}$, $\omega_{\text{rot}} = 58 \pm 1.5 \text{ cm}^{-1}$, $\xi \sim 0.06$, and α/β in the range $0-7 \text{ kg cm}^{-2} \text{ }^\circ\text{K}^{-1}$ at $300 \text{ }^\circ\text{K}$. From Eqs. (1) and (2), assuming the same values of ω_{rot} and $\partial\langle\theta^2\rangle/\partial T|_V^{\text{int}}$ for K_2ReCl_6 and using the experimental data in Table I, it follows that $\xi = 0.0564 - 0.0011 \alpha/\beta$.

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That is, for α/β between 0 and 7, $\xi \sim 0.05$. This is a very reasonable result considering the limitations of the model.

The second result is that the π -bonding destruction model, previously shown to provide a self-consistent analysis of NQR frequency data in K_2PtCl_6 , K_2IrCl_6 , and K_2OsCl_6 , is also able to account for the NQR data in K_2ReCl_6 .

Lastly, let us consider the question of the effect on the NQR frequency data of the softening of the rotary lattice mode that accompanies the phase transition at $110.9 \text{ }^\circ\text{K}$. Since, for the data that we are able to analyze, $T - T_c > 165 \text{ }^\circ\text{K}$, a high-temperature approximation of the form¹⁰

$$\omega_{\text{rot}}^2 = \omega_0^2 + \gamma T^{1/2}$$

will be considered. The necessity for the inclusion of the term ω_0^2 has already been stated by O'Leary¹—there is only a small density of states available near $\vec{k} = 0$ and it is only those phonons for which $\vec{k} \approx 0$ whose energy approaches zero at the transition. According to O'Leary, $\omega_0 \approx 33 \text{ cm}^{-1}$. Assuming this value of ω_0 , and taking $\omega_{\text{rot}} = 60 \text{ cm}^{-1}$ at $350 \text{ }^\circ\text{K}$ gives a value for γ . Using this value of γ and $T = 275 \text{ }^\circ\text{K}$ gives $\omega_{\text{rot}} \sim 58 \text{ cm}^{-1}$. That is, the rotary mode only softens by $\sim 2 \text{ cm}^{-1}$ over the temperature range studied. An effect of this magnitude is within the uncertainty inherent in our simple model.

The third conclusion to be taken from this study is that softening of the rotary lattice mode may safely be neglected over the temperature range of our suggested interpretation.

To summarize, we have shown that volume effects are important in K_2ReCl_6 . By invoking a simple model to describe the destruction of π bonding by the lattice vibrations we have shown that a self-consistent description of the NQR-frequency data in K_2PtCl_6 , K_2IrCl_6 , K_2OsCl_6 , and K_2ReCl_6 can be obtained. For temperatures between 275 and $350 \text{ }^\circ\text{K}$, the effect of the softening of the rotary lattice mode associated with the structural phase transition at $110.9 \text{ }^\circ\text{K}$ is relatively small. These results in no way invalidate the suggestion of O'Leary¹ concerning the usefulness of the NQR technique as a tool for the detection of soft librational modes. They do, however, suggest that a correct quantitative analysis near the phase transition must await a measurement of the volume effects.

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

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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 paper⁵ which presents the preliminary results of a systematic study of the NQR pressure dependence in these salts.

The "raison d'être" 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 $R_2\text{MX}_6$ salts. The volume expansion coefficient α for K_2SnBr_6 was found by Galloni

*et al.*⁶ to be $155 \times 10^{-6} \text{ }^\circ\text{K}^{-1}$. 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 $\sim 125 \times 10^{-6} \text{ }^\circ\text{K}^{-1}$, thus partially confirming the similarity.

Compressibilities are also fairly well known. The lattice dynamics calculation of Ref. 2 yields a longitudinal sound velocity of $\sim 3.4 \times 10^5 \text{ cm/sec}$ and a transverse sound velocity of $\sim 1.3 \times 10^5 \text{ cm/sec}$. Combining these velocities with the known density⁷ of 3.325 g/cm^3 gives a compressibility β of $3.2 \times 10^{-6} \text{ cm}^2\text{kg}^{-1}$. Thus, the thermodynamic parameter α/β in fact has a value of $\sim 40 \text{ kg cm}^{-2} \text{ }^\circ\text{K}^{-1}$ 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 ($M = \text{Pt, Ir, Os, Re}$) radical by Cotton and Harris.⁸ These calculations indicate that the hole in the chlorine $3p_\pi$ orbitals is about $0.05e$ 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