

reasonable.¹³ In fact, with $Z_1=0$ for a neutral Pd atom and with $Z_2=3$ for an unscreened Yb³⁺ ion, one finds from the above $A_4\langle r^4 \rangle = -10.7 \text{ cm}^{-1}$ and $A_6\langle r^6 \rangle = -0.06 \text{ cm}^{-1}$. Such excellent agreement with experiment is probably coincidental. However, in most cases one finds that such simple calculations will reproduce the order of magnitude and the correct sign for the crystal field parameters,¹⁴ and the present result is in line with that general feature. It may also be noted that simple nearest-neighbor calculations have recently been very successful in calculating crystal field parameters for a number of rare-earth metallic compounds.¹ The apparent success of what seems to be a naive model is not understood. In view of the present agreement with experiment, we have made no attempt to interpret the data in terms of more sophisticated approaches, such as in Ref. 2.

In low-field spectra ($H_{\text{ext}} \leq 5 \text{ kOe}$) only one very

broad line is observed. Assuming that the broadening is due to slow spin relaxation processes, we have analyzed the spectra with the simple two-level relaxation expression¹⁵ appropriate for an isolated Kramers doublet, since 5 kOe is insufficient to mix an appreciable fraction of the Γ_8 level. An example is given in Fig. 4. This analysis provides an electronic spin-relaxation time $\tau_R \approx 4 \times 10^{-11} \text{ sec}$, roughly independent of H_{ext} and T . These spectra were analyzed assuming complete polarization, i. e., that the intensity of the $\Delta I_z = 0, \pm 2$ lines was zero. Attempts to fit with a full five line spectra were quite unsuccessful. This indicates that the observed magnetic anisotropy at higher fields is due solely to the anisotropy of the Γ_8 level which is admixed into the ground state by the applied field. This is also indicated by the increase in the intensity of the $\Delta I_z = 0$ transition as the external field is increased (see Fig. 1).

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¹K. C. Turberfield, L. Passel, R. J. Birgeneau, and E. Bucher, Phys. Rev. Letters **25**, 752 (1970); J. Appl. Phys. **42**, 1746 (1971).

²G. Williams and L. L. Hirst, Phys. Rev. **185**, 407 (1969).

³D. Davidov, R. Orbach, C. Rettori, D. Shaltiel, L. J. Tao, and B. Ricks, Phys. Letters **37A**, 361 (1971); **35A**, 339 (1971).

⁴L. R. Harris and G. V. Raynor, J. Less-Common Metals **9**, 263 (1965).

⁵A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970), pp. 721-732.

⁶K. R. Lea, H. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

⁷H. Eicher, Z. Physik **169**, 178 (1962).

⁸M. T. Hutchings, Solid State Phys. **16**, 277 (1966).

⁹J. M. Baker, W. B. J. Blake, and G. M. Copland, Proc. Roy. Soc. (London) **A309**, 119 (1969).

¹⁰W. E. Gardner, J. Denfold, and I. R. Harris, J. Phys. (Paris) **32**, (1971).

¹¹A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

¹²R. D. Hutchens, V. U. S. Rao, J. E. Greedau, W. E. Wallace, and R. S. Craig, J. Appl. Phys. **42**, 1293 (1971).

¹³A similar argument has been used for the rare-earth-Ni₂ system by B. Bleaney, Proc. Roy. Soc. (London) **276**, 28 (1963).

¹⁴For a notable exception, see Ref. 2.

¹⁵I. Nowik and H. H. Wickman, Phys. Rev. Letters **17**, 949 (1966).

Spin-Wave Approach to One-Dimensional Antiferromagnetic CsNiCl₃ and RbNiCl₃

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The spin-wave approximation is applied to linear-chain antiferromagnets CsNiCl₃ and RbNiCl₃. The susceptibility as well as the zero-temperature magnetic moment is calculated. There is good agreement between the experimental results and the theoretical calculations.

Recently attention has been focused on substances that exhibit one-dimensional properties,¹ such as CsNiCl₃ and RbNiCl₃. These have chains of octahedrally coordinated Ni²⁺ ions along the *c* axis. At low temperatures and above their three-dimensional ordering temperatures (11 and 4.5 °K for RbNiCl₃ and CsNiCl₃, respectively) these com-

pounds show many of the characteristics of linear antiferromagnets.² A very interesting result has been obtained by Cox and Minkiewicz.³ They showed that the magnitude of the Ni²⁺ moment in CsNiCl₃ extrapolated to 0 °K is $(1.05 \pm 0.1) \mu_B$ (μ_B is the Bohr magneton). They attributed it to a very substantial zero-point deviation. In this paper we re-

port the theoretical calculations of the magnetic susceptibility and the magnetic moment of RbNiCl_3 and CsNiCl_3 . This has been done using a one-dimensional spin-wave approximation, which explains satisfactorily the experimental results.

The magnetic properties of these compounds at low temperatures can be described in terms of an effective spin Hamiltonian of the form

$$\mathcal{H} = \sum_{i,j}' J \vec{S}_i \cdot \vec{S}_j - D \sum_i S_{iz}^2 - g_{\parallel} \mu_B H_0 \sum_i S_{iz}, \quad (1)$$

where S is of magnitude 1, D is the single-ion anisotropy, g_{\parallel} is the gyromagnetic factor ($g_{\parallel} = 2.24$ for CsNiCl_3 and $g_{\parallel} = 2.21$ for RbNiCl_3), and H_0 the external magnetic field. This Hamiltonian was analyzed using the spin-wave approximation. The magnon energy was obtained with the Holstein-Primakoff approximation and considering only the nearest-neighbor interaction along the c axis⁴:

$$\begin{aligned} \epsilon_k^{\pm} &= (A^2 - B_k^2)^{1/2} \pm g_{\parallel} \mu_B H_0, \\ A &= D + 2J, \\ B_k &= 2J \cos(ka), \end{aligned} \quad (2)$$

where a is the distance between Ni^{2+} along the c axis.

The partition function is given by

$$\begin{aligned} Z &= e^{-\beta E_0} \exp\left\{-\beta \sum_k [(A^2 - B_k^2)^{1/2} - A]\right\} \\ &\quad \times \prod_k (1 - e^{-\epsilon_k^+ \beta})^{-1} (1 - e^{-\epsilon_k^- \beta})^{-1}, \end{aligned}$$

$$\beta = \frac{1}{k_B T}, \quad (3)$$

$$E_0 = -2N_0(D+J),$$

where N_0 is the number of magnetic atoms in one sublattice.

Then one obtains for the sublattice magnetization

$$N_0 \langle S_z \rangle = \pm N_0 g_{\parallel} \mu_B \mp \frac{g_{\parallel} \mu_B}{2} \sum_k \left(\frac{A}{(A^2 - B_k^2)^{1/2}} - 1 \right)$$

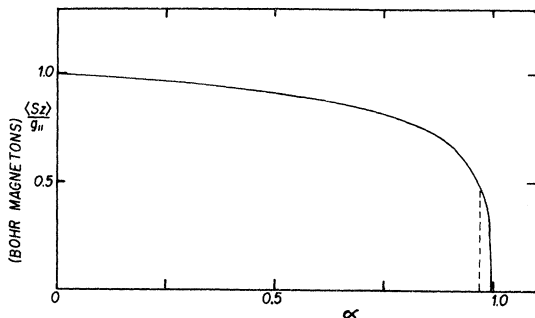


FIG. 1. Zero-temperature magnetic moment divided by the gyromagnetic factor plotted vs $\alpha = 4J^2/(2J+D)^2$. The line indicates the experimental value for CsNiCl_3 .

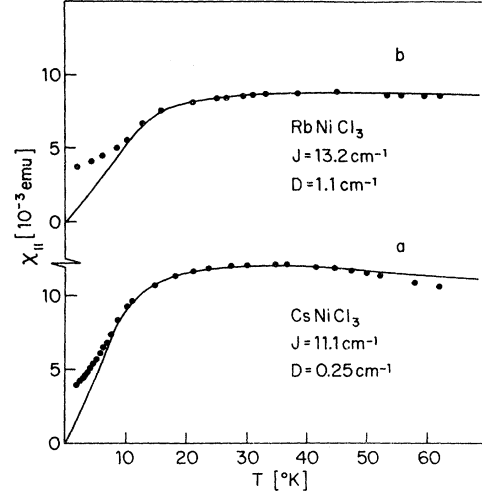


FIG. 2. (a) Parallel susceptibility vs temperature for CsNiCl_3 . (b) Parallel susceptibility vs temperature for RbNiCl_3 . Black dots represent the experimental results of Achiwa (Ref. 2). The solid lines are our theoretical fit. The points below 4.5 °K for CsNiCl_3 and 11 °K for RbNiCl_3 correspond to the three-dimensional order and are not fitted by our model.

$$\begin{aligned} & \mp \frac{g_{\parallel} \mu_B}{2} \sum_k \frac{A}{(A^2 - B_k^2)^{1/2}} \left(\frac{1}{e^{\epsilon_k^+ \beta} - 1} + \frac{1}{e^{\epsilon_k^- \beta} - 1} \right) \\ & - \frac{g_{\parallel} \mu_B}{2} \sum_k \left(\frac{1}{e^{\epsilon_k^+ \beta} - 1} - \frac{1}{e^{\epsilon_k^- \beta} - 1} \right). \end{aligned} \quad (4)$$

The sublattice magnetization at zero temperature for the linear chain is equal to

$$N_0 \langle S_z \rangle_{T=0} = \frac{3}{2} N_0 g_{\parallel} \mu_B - \frac{N_0 g_{\parallel} \mu_B}{\pi} K(\alpha), \quad (5)$$

$$K(\alpha) = \int_0^{\pi/2} \frac{dx}{(1 - \alpha \cos^2 x)^{1/2}}, \quad \alpha = \frac{4J^2}{(D+2J)^2}.$$

$K(\alpha)$ remains finite for D different from zero.

In Fig. 1 the magnetic moment is plotted as a function of α . For $\alpha=1$ there is a singularity. Also, if the second term in Eq. (5) is larger than the first term the spin-wave approximation breaks down. This occurs for very small values of D .

The parallel susceptibility calculated from Eq. (3) is given by

$$\chi_{\parallel}|_{H_0=0} = 2(g_{\parallel} \mu_B) \beta \sum_k \frac{e^{\epsilon_k \beta}}{(e^{\epsilon_k \beta} - 1)^2}. \quad (6)$$

Using the above formula we fitted the susceptibility measurements of Achiwa.²

The experimental results and theoretical calculations are shown in Figs. 2(a) and 2(b). The values obtained from the fitting for the single-ion anisotropy and the exchange integral are shown in Table I.

TABLE I. Values for single-ion anisotropy and the exchange integral.

	D (cm ⁻¹)	J (cm ⁻¹)
RbNiCl ₃	1.1 ± 0.3	13.2 ± 0.5
CsNiCl ₃	0.25 ± 0.1	11.1 ± 0.3

There is poorer agreement between experiment and theory in the high-temperature region since the magnon-magnon interaction cannot be disregarded in this region.

A striking result is obtained for the zero-temperature magnetic moment of CsNiCl₃. We obtained theoretically

$$\langle S_z \rangle_{T=0} = (1.05 \pm 0.07) \mu_B$$

(the uncertainty in the above values results from the lack of sensitivity of the susceptibility to small changes in the fitting parameters D and J). The experimental result is $(1.05 \pm 0.1) \mu_B$.³ Thus the agreement is extraordinary. For RbNiCl₃ we ob-

tained

$$\langle S_z \rangle_{T=0} = (1.33 \pm 0.1) \mu_B.$$

This value is lower than the experimental result $[(1.6 \pm 0.15) \mu_B]$ reported in the literature,⁵ but since the measurements were done on powder samples one expects that in single crystals a lower value will be obtained, as was the case with CsNiCl₃.³ Thus the low value of the magnetic moment at zero temperature is caused by the zero-point deviation and is a one-dimensional phenomenon. Although at zero temperatures this compound is a three-dimensional antiferromagnet, the antiferromagnetic alignment along the chain persists and the interchain interaction only caused the setup of a triangular array below 4.5 °K.

The fact that spin waves in one dimension persist above the three-dimensional phase transition has been observed by neutron scattering in CsMnCl₃ · 2D₂O by Skalyo *et al.*¹ Here we have shown that the spin-wave approximation can be used to treat the elementary excitations in one-dimensional systems with finite anisotropy.

¹T. Smith and S. A. Friedberg, Phys. Rev. 176, 660 (1968); R. Dingle, M. E. Lines, and S. L. Holt, *ibid.* 187, 643 (1969); J. Skalyo, Jr., G. Shirane, S. A. Friedberg, and H. Kobayashi, Phys. Rev. B 2, 4632 (1970).

²N. Achiwa, J. Phys. Soc. Japan 27, 561 (1969).

³D. E. Cox and V. J. Minkiewicz, Phys. Rev. B 4, 2209 (1971).

⁴R. Kubo, Phys. Rev. 87, 568 (1952); F. Keffer, in

Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1966), Vol. XVII; L. R. Walker, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. I. We have used the transformation given by L. R. Walker for the one-ion terms.

⁵V. J. Minkiewicz, D. E. Cox, and G. Shirane, Solid State Commun. 8, 1001 (1970).