Theoretical and experimental study of the magnetic properties of the singlet-ground-state system $Cu(NO_3)_2 \cdot 2.5H_2O$: An alternating linear Heisenberg antiferromagnet

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The thermodynamic properties of $Cu(NO_3)_2 \cdot 2.5H_2O$ are compared with calculated properties of the one-dimensional alternating Heisenberg antiferromagnet as described by the Hamiltonian: $\mathcal{H} = -2J \sum_n (\vec{S}_{2n} \cdot \vec{S}_{2n+1} + \alpha \vec{S}_{2n} \cdot \vec{S}_{2n-1}) - g\mu_B \sum_n \vec{H} \cdot \vec{S}_n$, with $\alpha = 0.27$ and $J/k = -2.6$ K. The thermodynamic properties, obtained from exact calculations of the eigenvalues of $\mathcal{H}$, for 2, 4, 6, 8, 10, and 12 spins, have been extrapolated to $n = \infty$ to obtain the behavior of the infinitely long alternating chain.

I. INTRODUCTION

In the past, theorists have paid much attention to one-dimensional (1D) magnetic systems. It proved possible to obtain rigorous mathematical solutions for 1D systems in contrast to most two-dimensional (2D) and three-dimensional (3D) systems.[1] Experimentalists successfully searched for quasi-1D systems in real crystals, few of which approximate the ideal theoretical model very well.[2]

Interest has evolved in the direction of more complicated 1D systems (like alternating chains[3-13]) and also in the direction of the influence of weak interchain couplings. In real crystals, weak interchain interactions are always present. Their presence will induce a transition to a 3D long-range-ordered state at nonzero temperature. In the ordered state, large field-dependent spin reduction[14,15] and an increase of the transition temperature towards higher fields are observed.[16,17]

Recent interest in quasi-1D organic compounds[18-20] stimulated theorists to consider the alternating antiferromagnetic (AF) linear chain. Some of these compounds contain regular $S = \frac{1}{2}$ AF chains above the so-called "spin-Peierls" transition temperature T_c. At T_c a temperature-dependent dimerization of the chain sets in, leading to a system of $S = \frac{1}{2}$ alternating chains for $T < T_c$. Below T_c, the interaction J within the dimers (pairs) is stronger than the interaction J' between the dimers. These "spin-Peierls" salts are not very suitable for the experimental study of alternating chains. The exchange integrals J and J' in the "spin-Peierls" salts known at present are relatively strong, so that only "low-field" properties can be investigated experimentally with the available magnetic fields. Moreover, a direct comparison between the experimental data and the theoretical results is hindered by the fact that both J and J', and consequently the alternation ratio $J'/J = \alpha$, are temperature dependent.

Recently, we have proved that $Cu(NO_3)_2 \cdot 2.5H_2O$ contains a system of weakly coupled $S = \frac{1}{2}$ alternating Heisenbert AF chains (with $J/k = -2.60$ K and $\alpha = 0.27$) (Refs. 21 and 22, hereafter referred to Papers I and II). The alternation ratio α of this alternating chain is temperature independent. The relatively small exchange constants J and αJ provide the possibility of studying the thermodynamic properties over the whole interesting field range (up to 70 kOe i.e., $h \equiv g\mu_B H/|J| \approx 4$). We have, in fact, already published most of our experimental results on $Cu(NO_3)_2 \cdot 2.5H_2O$; such as the specific heat in external field, isothermal magnetization, susceptibility, and cooling curves $T_S(H)$.[21-24] These data have been interpreted in terms of the effective spin-$\frac{1}{2}$ formalism proposed by Tachiki.[25] Tachiki's theory was found to describe adequately the temperature dependences of thermodynamic quantities. Discrepancies arise in describing the field dependences of quantities like $T_S(H)$, $\chi_S(H)$, and $M_T(H)$. It was argued that these discrepancies originate from the simplification introduced by using the effective spin formalism. In this paper, we will discuss thermodynamic properties of the alternating Heisenberg AF chain (with $\alpha = 0.27$), obtained by using the method introduced by Bonner and Fisher.[26] This method is discussed in Sec. II. In the subsequent sections, calculated thermodynamic properties are given and compared to the experimental data of $Cu(NO_3)_2 \cdot 2.5H_2O$. In Sec. XI, we pay some attention to the shortcomings of the effective spin model.[21,27] We often refer to the paper of Perk *et al.*[13] on the X-Y alternating chain. They calculate the zero-temperature magnetization and susceptibility and the specific heat in external field. They also study the influence of anisotropy in the X-Y exchange interaction. Their work inspired us to perform the calculations presented here to get a better theoretical description of the properties of $Cu(NO_3)_2 \cdot 2.5H_2O$.

II. ALTERNATING HEISENBERG ANTIFERROMAGNETIC LINEAR CHAIN

The magnetic system which is the subject of our theoretical study is described by the following Hamiltonian:

$$\mathcal{H} = -2J \sum_{i=1}^{n/2} (\vec{S}_{2i} \cdot \vec{S}_{2i+1} + \alpha \vec{S}_{2i} \cdot \vec{S}_{2i-1}) - g\mu_B \sum_{j}^{n} \vec{H} \cdot \vec{S} \,, \tag{1}$$

with $S = \frac{1}{2}$.

Depending on the boundary conditions, this Hamiltonian describes an open chain or a ring of n spins. The eigenvalues of the Hamiltonian for finite chains as well as for rings are computed exactly for $n = 2, 4, \ldots, 10$ and $n = 2, 4, \ldots, 12$, respectively. From the energy spectra, the partition function and, consequently, thermodynamic properties in zero and external field of the finite systems can be easily calculated. Extrapolating these data to $n = \infty$ yields accurate estimates for the properties of the infinitely long chain. This method was first applied by Bonner and Fisher[26] to the regular $S = \frac{1}{2}$ Heisenberg AF chain. Later, Duffy and Barr[6] applied it to the alternating $S = \frac{1}{2}$ Heisenberg AF chain. They confined their calculations to the zero-temperature magnetization and zero-field properties. One of us[28] has demonstrated the applicability of the method to chains with larger spin values. Bonner and Friedberg[29,30] have performed such calculations on AF spin ladders and alternating AF chains to describe their zero-field specific heat and susceptibility data of $Cu(NO_3)_2 \cdot 2.5H_2O$. Their calculations were restricted, however, to clusters with up to 6 spins and mainly to low-field properties. We have extended these calculations to obtain the properties of the alternating AF chain in the external field. The characteristics of this system are found to be more clearly demonstrated when an external field is applied. To get reliable results on these properties, the calculations were done for larger clusters having up to 12 spins. These calculations were executed for fixed α values. We have confined this study to the alternating AF chain with $\alpha = 0.27$, which value is based upon determinations of J and $\alpha J(J')$ as described in Paper I. It will become clear from the comparison of theory and experiment that the intrachain interactions in $Cu(NO_3)_2 \cdot 2.5H_2O$ indeed show an alternation parameter of 0.27 ± 0.02.

III. ENERGY SPECTRUM

For the case $\alpha = 0$, the Hamiltonian [Eq. (1)] describes an assembly of noninteracting AF spin pairs. The energy spectrum of such a system consists of a singlet ground state and an excited triplet $2|J|$ higher in energy. Numerical calculations show that in zero field, an infinitely long alternating chain with $0 < \alpha < 1$ has a nondegenerate singlet ground state and an infinite set of continuous exciton bands.[6] These bands are already clearly visible in the energy spectrum of the six-spin cluster given in Fig. 1. The width of the bands is of the order of $2\alpha|J|$,[11] while the first excited band is separated from the singlet ground state by an energy gap ΔE of about $(2-\alpha)|J|$.

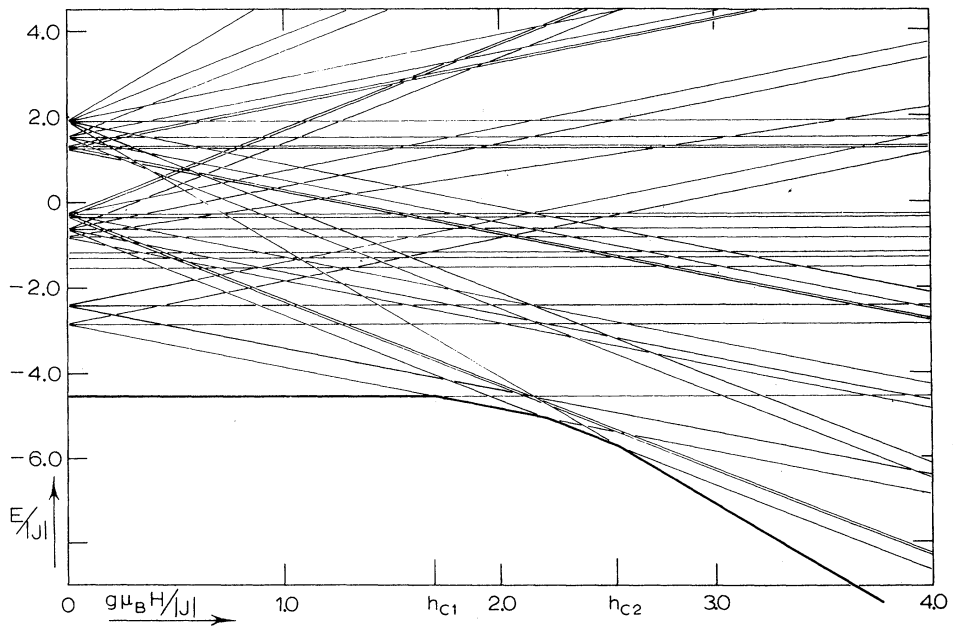

FIG. 1. Energy spectrum of an alternating ring of six spins $S = \frac{1}{2}$ as a function of the applied field $h \equiv \mu_B g H/|J|$. The interactions between the spins are described by the Hamiltonian [Eq. (1)] given in the text.

From Fig. 1, it is seen that when an external field is applied, this situation changes drastically. Around $h \equiv g\mu_B H/|J| \approx 2 + 0.5\alpha$, a set of bands again occurs. In the field region $h_{c1} < h < h_{c2}$, the lowest energy states form, for $n = \infty$, a continuous band, which has a width of about $2\alpha|J|$ and is separated by about $(2-\alpha)|J|$ in energy from the lowest excited band. At each field in between h_{c1} and h_{c2}, the ground state of the infinite chain is degenerate, in contrast to the situation at fields outside this region, where the ground state is always a singlet. Therefore, weak interchain interactions, always present in real crystals, can induce long-range order only at fields in (or very near) this anomalous region. This was experimentally proved in $Cu(NO_3)_2 \cdot 2.5H_2O$,[22,24] and also in $Ni(C_5H_5NO)_6(ClO_4)_2$.[31]

IV. ZERO-FIELD SPECIFIC HEAT AND SUSCEPTIBILITY

We have calculated the zero-field specific heat of the alternating AF chain with $\alpha = 0.27$. The zero-field specific-heat curve shows a broad anomaly which has a maximum of $C/R = 0.49$ around $t \equiv kT/|J| = 0.70$. The thermodynamic quantities in zero field can be obtained very accurately because the convergence to $n = \infty$ of the calculated data for finite n is very fast. This rapid convergence is illustrated by the fact that the specific heat of the six-spin chain and of the infinite chain are equal to within 0.5%. On the other hand, it is seen that the maximum of the specific-heat curve (for $\alpha = 0.27$) is only 5% lower than the maximum for the isolated spin pair ($\alpha = 0$). In other words, the zero-field specific heat is not very sensitive to the value of α (at least for small α values). A similar dependence on α is found for the zero-field susceptibility. In weak fields, the weaker interaction αJ can be considered as a perturbation on the isolated pair system. In the anomalous region, however, αJ plays a major role in the thermodynamic behavior of the alternating chain. Roughly speaking, from zero-field measurements, one learns about the strong interaction J, while in the anomalous region, properties for $T \leq \alpha|J|/k$ are determined mainly by the weaker interactions αJ. This will be illustrated in the next sections. Friedberg and Raquet[32] had already measured $C_{H=0}(T)$ and $\chi_{H=0}(T)$ of $Cu(NO_3)_2 \cdot 2.5H_2O$ in 1968. Bonner[29] analyzed these data by comparing them to the results of six-spin clusters with different α values. This is clearly justified by the fast convergence, as discussed above. The weak sensitivity of the zero-field properties on the ratio α, for $\alpha \leq 0.5$ implies that α cannot be obtained accurately from zero-field experiments. In view of this, the value of $\alpha = 0.36$ obtained by Bonner can be considered to be reasonably in agreement with our result $\alpha = 0.27 \pm 0.02$.

V. ZERO-TEMPERATURE MAGNETIZATION

One-dimensional magnetic systems show a characteristic field dependence of their zero-temperature magnetization.[33] The typical $M_{T=0}(H)$ curve of an alternating $S = \frac{1}{2}$ Heisenberg AF chain is of course dependent on the value of α.[6] In Fig. 2, the calculated $M_{T=0}(H)$ curves for $\alpha = 0$, $\alpha = 0.27$, and $\alpha = 1.0$ are shown.

The limiting case $\alpha = 0$ corresponds to the isolated AF pair system, while the other limit evidently represents the regular $S = \frac{1}{2}$ AF linear

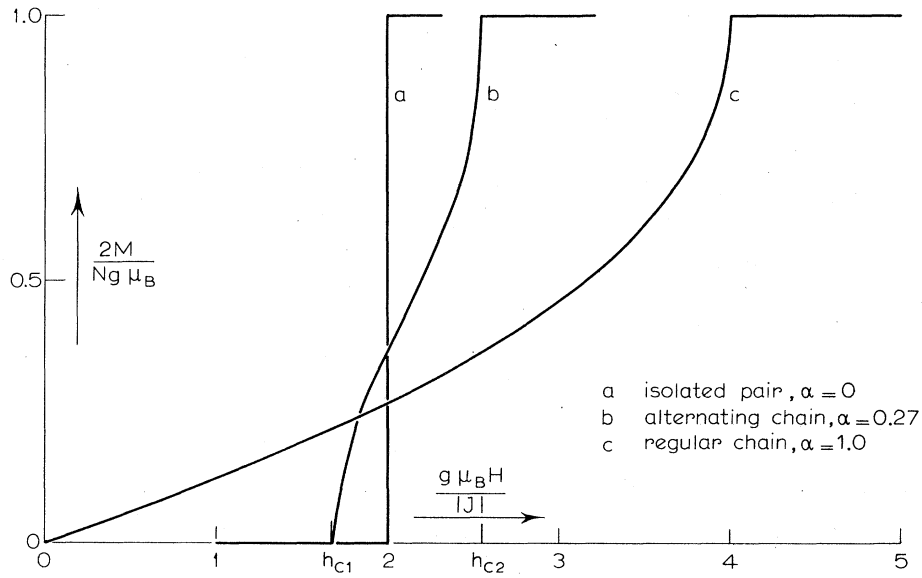

FIG. 2. Zero-temperature magnetization of the alternaing Heisenberg AF chain vs the applied field for three different values of the alternation parameter ($\alpha = 0$, $\alpha = 0.27$, and $\alpha = 1.0$). The critical fields of curve b are $h_{c1} = 1.675$ and $h_{c2} = 2.540$.

chain.[26,34] For systems with $\alpha \neq 0$, two critical fields h_{c1} and h_{c2} can be defined. For $T=0$ below h_{c1}, the magnetization is zero, while above h_{c2}, it is saturated. In Fig. 1, h_{c1} and h_{c2} are indicated. The value of the upper critical field is easily shown to be given exactly by $h_{c2}=2(1+\alpha)$. This yields for $\alpha=0.27$, $h_{c2}=2.54$. An exact analytical expression for h_{c1}, however, cannot be obtained. From Fig. 1, it is clear that this critical field h_{c1} is directly related to the energy gap in zero-field ΔE between the ground state and the first excited energy band. The dependence of this energy gap on the alternation ratio α has been a subject of several theoretical studies. Drawid and Halley[35] have recently shown that the various theoretical results show large discrepancies. Our study of the energy spectrum (Fig. 1) of small clusters as a function of n and the extrapolation to infinite systems leads to an accurate estimate of ΔE especially for chains with strong alternation (small α). We obtained for $\alpha=0.27$ a value of $\Delta E/N|J| \equiv h_{c1}=1.675$. Bonner and Blöte[36] are currently investigating by this method the ground-state energy and the energy gap as a function of the alternation parameter α. Brooks Harris[11] gives a high-order perturbation theoretical expression for both the ground-state energy

$$E_0/N|J| = -\tfrac{3}{2} - \tfrac{3}{16}\alpha^2 - \tfrac{3}{64}\alpha^3 + \cdots ,$$

and an expression for the energy gap

$$\Delta E/N|J| = 2 - \alpha - \tfrac{3}{4}\alpha^2 + \tfrac{1}{16}\alpha^3 + \cdots .$$

Inserting the value $\alpha=0.27$, one obtains $\Delta E/N|J| = 1.677$, which is in perfect agreement with our numerical result given above.

VI. MAGNETIZATION ISOTHERMS FOR $T \neq 0$

In Fig. 3, some calculated magnetization isotherms of the alternating chain are shown for the interesting field range $0 \leq h \leq 4$, for $0 \leq kT/|J| < 1.5$, together with our experimental data on $Cu(NO_3)_2 \cdot 2.5H_2O$ for several temperatures. The magnetization of $Cu(NO_3)_2 \cdot 2.5H_2O$ has been deduced from proton resonance experiments. In the calculations, we have used the reported values of $Cu(NO_3)_2 \cdot 2.5H_2O$, $g_b = 2.33$, $J/k = -2.60$ K and $\alpha = 0.27$ (Paper I). In $Cu(NO_3)_2 \cdot 2.5H_2O$, the alternating chains are not perfectly isolated from each other. Weak interactions between the chains in the crystallographic a-c plane $J'_{a-c}/k \approx -0.05$ K and interactions between the chains along the b axis $J'_b/k \approx +0.05$ K are present (Paper II). These interactions have not been taken into account in the calculations. Considering these interactions in a molecular-field approach, the net effect would almost vanish because of the different signs of J'_b and J'_{a-c}.

From Fig. 3, it is seen that there is a perfect agreement between the measured $M_T(H)$ curves and the calculated ones for temperatures above $T = 0.25$ K ($t = kT/|J| \geq 0.1$). In the field and temperature range near the phase boundary (Paper II), small discrepancies exceeding both the experimental and theoretical accuracy are observed. It must be stressed that the agreement mentioned

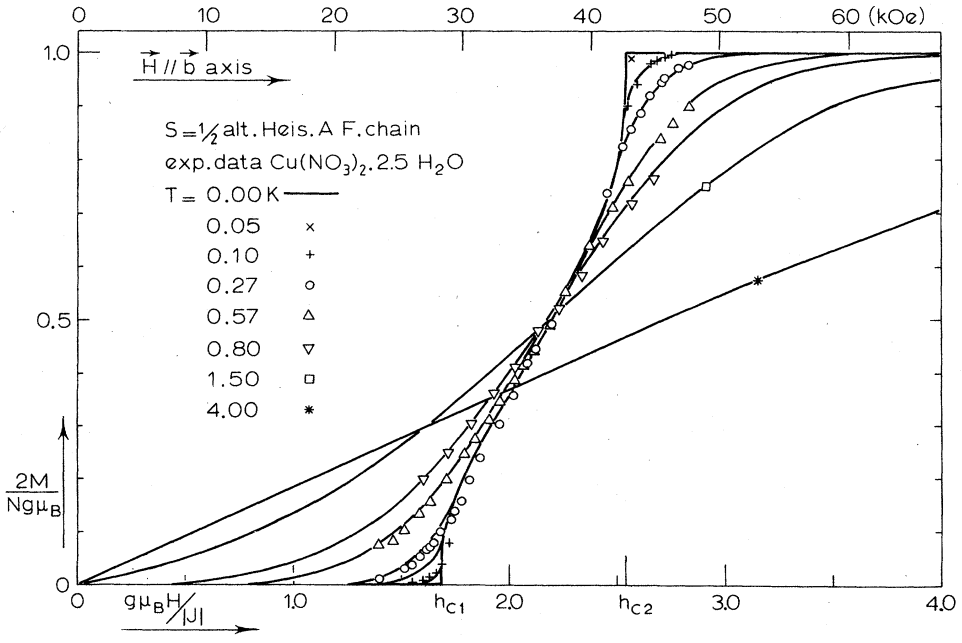

FIG. 3. Calculated magnetization isotherms of the alternating Heisenberg AF chain with $\alpha = 0.27$ and the experimentally determined magnetization of $Cu(NO_3)_2 \cdot 2.5H_2O$ for several temperatures. The experimental data were obtained from NMR experiments.

above between theory and experiment is obtained by using only the independently measured values of g, J', and J. This confirms the accuracy of our determinations of g, J', and J discussed in Paper I. (see Table I in Sec. XII).

All thermodynamic properties in an external field show a faster convergence to $n=\infty$ when they are calculated from the energy eigenvalues of closed chains (rings) than when the calculations are performed on open chains. This is also true for the thermodynamic properties in an external field of the regular $S=\frac{1}{2}$ AF Heisenberg chain and the regular $S=\frac{1}{2}$ anisotropic ($J_\perp = 2J_\parallel$) AF chain, studied by Henkens[33] and Diederix,[22] respectively. One of us[28] concluded that for *zero-field* properties, however, better convergent results could be obtained from open-chain calculations.

The calculated magnetization (and also other quantities) versus n rapidly converges as n increases, at least for high relative temperatures ($kT/|J| \gtrsim 0.01$).

For temperatures below $kT/|J| < 0.05$, the extrapolations become very inaccurate. Therefore, to obtain the zero-temperature curve $M_0(H)$, we have used a different procedure. This curve, discussed in the previous section, was obtained by connecting the midpoints of the magnetization steps of the finite chains and extrapolating these results of $n=2,\ldots,12$ to $n=\infty$. This method was also used by Bonner and Fisher[26] to obtain the zero-temperature magnetization curve of the regular $S=\frac{1}{2}$ Heisenberg AF chain. Their result agrees very accurately with Griffiths'[34] exact results.

VII. FIELD DEPENDENCE OF THE SUSCEPTIBILITY

The differential susceptibility is directly related to the magnetization: $\chi = (\partial M/\partial T)_{S \text{ or } T}$. However, depending on the experimental conditions, the adiabatic or the isothermal differential susceptibility is measured. We measured the susceptibility of $Cu(NO_3)_2 \cdot 2.5H_2O$, using the mutual inductance technique. The frequency of the applied oscillating field (320 Hz) proved to be much larger than the inverse of the electron spin-lattice relaxation time.[37,38] Consequently, we obtained the adiabatic susceptibility. The dc field, however, was varied under isothermal condition. The results are shown in Fig. 4 together with the theoretical zero-temperature curve. [At $T=0$, $\chi_S(H)$ and $\chi_T(H)$ are equal]. This theoretical curve was obtained by differentiation of the calculated zero-temperature magnetization isotherm. A small molecular field was incorporated to fit the theoretical and experimental critical field h_{c2}. The theoretical and experimental values for the critical field h_{c1} agree perfectly. This molecular field in $Cu(NO_3)_2 \cdot 2.5H_2O$ originates from the interchain interactions J_b' and J_{a-c}'' (although they partially compensate each other) and from the small demagnetization field. The latter is estimated from the shape of the sample to be about 60 Oe for full magnetization.[39]

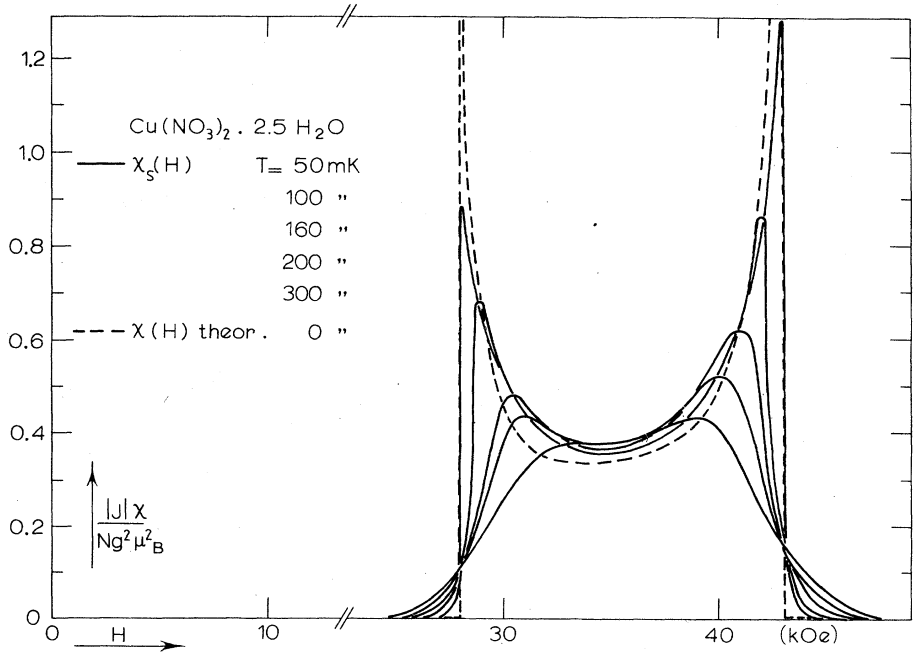

FIG. 4. Measured field dependences of the adiabatic susceptibility $\chi_S(H)$ of $Cu(NO_3)_2 \cdot 2.5H_2O$. During the measurements the "static" applied field H was varied under isothermal conditions at the temperatures listed in the figure. The susceptibility at low temperatures drops sharply outside the anomalous region. The calculated field dependence of the susceptibility at $T=0$ of the isolated alternating chain (with $\alpha = 0.27$) is shown by the dashed curve.

Although the theoretical curve must not be considered to be very accurate, it is reliable enough to justify a comparison with the experimental results. In this field region at 50 mK, χ has reached its zero-temperature value, and thus can be compared to the zero-temperature curve. Between 30 and 40 kOe, the experimental χ remains larger than the theoretical value. The difference between the two curves is attributed to the existence of long-range order below $T = 0.2$ K, as discussed in Sec. VIII. The qualitative agreement between the theoretical curve and, especially, the experimental 50-mK curve is very good. The peaks at the critical fields of the measured curve are limited because of the finite temperature. At still lower temperatures they will increase and eventually be limited by the demagnetization factor or interchain interactions J''. The observed peak at h_{c1} is, however, substantially lower and narrower than the peak at h_{c2}; the whole curve is asymmetric around the field $h_{1/2} = \frac{1}{2}(h_{c1} + h_{c2})$. These features are in striking agreement with the calculated curve. At the critical fields h_{c1} and h_{c2}, the slope of the susceptibility-versus-field curves increases towards lower temperatures (Fig. 4) leading for $T = 0$ to a discontinuous change of χ from zero, outside the field region $h_{c1} - h_{c2}$, to a nonzero value inside this field region. The calculated curve shows the same discontinuous behavior at both critical fields. Perk *et al.*[13] calculate for the isotropic alternating X-Y chain ($J_x = J_y$) that $\chi_0(H)$ shows power-$\frac{1}{2}$ singularities at the upper side of h_{c1} and at the lower side of h_{c2}, $\chi = 0$ for $h < h_{c1}$ and $h > h_{c2}$. When $J_x \neq J_y$, the susceptibility appears at *both* sides of h_{c1} and h_{c2}, a logarithmic behavior. The peaks at the critical fields of both the experimental and theoretical curves in Fig. 4 strongly resemble those of the isotropic alternating X-Y chain. This is additional evidence for the conclusion that both J and αJ are isotropic (Paper I).

VIII. TEMPERATURE DEPENDENCE OF $\chi_{S,H}$

The adiabatic differential susceptibility χ_S of $Cu(NO_3)_2 \cdot 2.5H_2O$ was also obtained as a function of temperature at $H = 36.8$ kOe ($\vec{H} \| \vec{b}$). $\chi(T)$ was again measured using the mutual-inductance technique. The frequency of the oscillating field was, at all temperatures, much higher than the inverse of the spin-lattice relaxation time, so that again adiabatic susceptibilities χ_S were measured. The mutual inductance was obtained in relative units. The mutual inductance for $\chi_S = 0$ was easily obtained by a reading at the lowest temperature (50 mK) at a field well above H_{c2} (see Fig. 4). The value of the external field at which these experiments were performed is just slightly higher than the field value at which the magnetization becomes temperature independent below $T \approx 1.5$ K and obtains half of its saturation value. Below $T \approx 1.5$ K, the occupation of the higher-energy bands is negligible and the susceptibility is fully determined by the occupation of the lowest-energy band. The results of the measurements on $Cu(NO_3)_2 \cdot 2.5H_2O$ are shown in Fig. 5. The drawn curve and the dot-dashed curve in this figure represent the calcu-

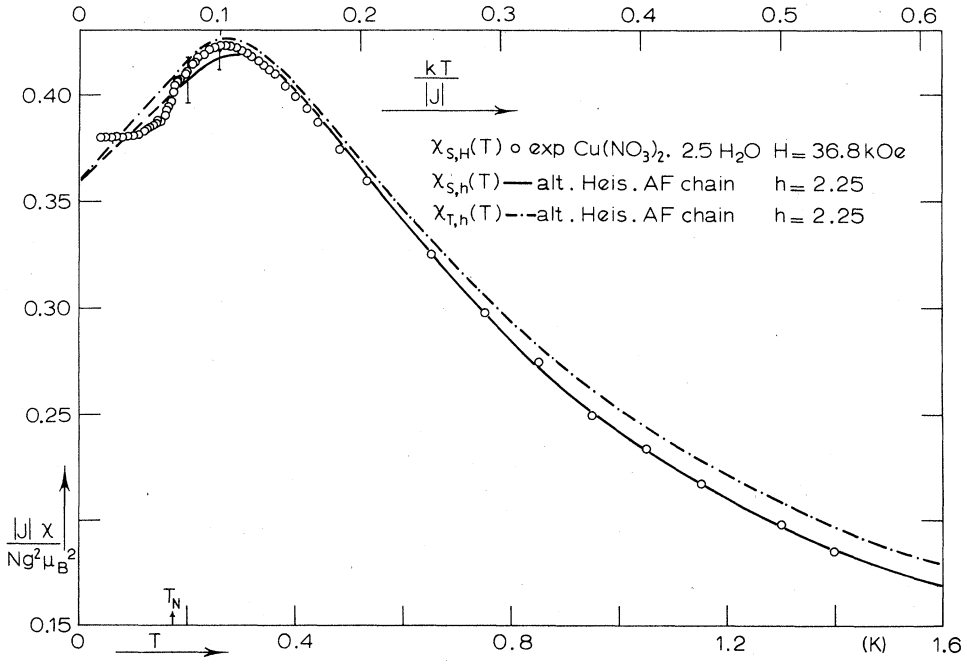

FIG. 5. The adiabatic susceptibility $\chi_{S,H}$ of $Cu(NO_3)_2 \cdot 2.5H_2O$ at $H = 36.8$ kOe for several temperatures. ———, —·—·— Calculated adiabatic susceptibility $\chi_{S,h}$ and isothermal susceptibility $\chi_{T,h}$, respectively, of the alternating Heisenberg AF chain with $\alpha = 0.27$ vs temperature at $\mu_B g H/|J| \equiv h = 2.25$.

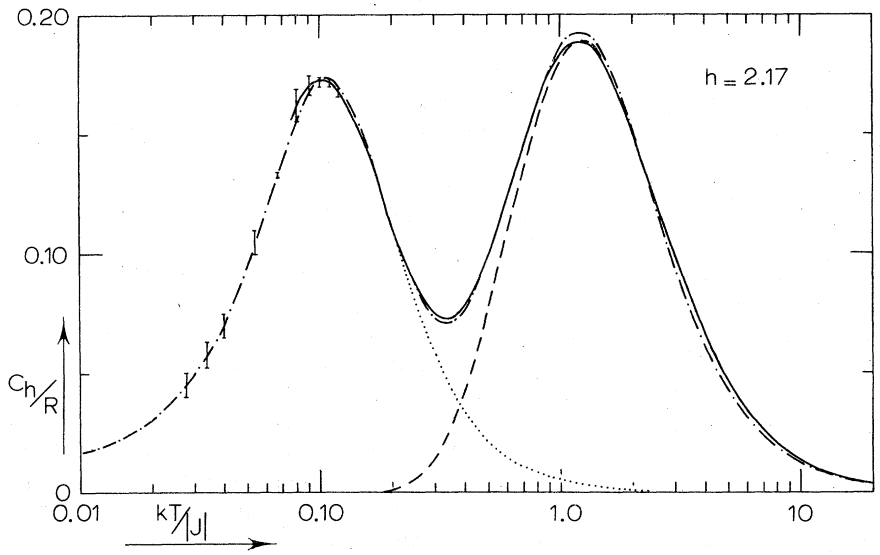

FIG. 6. (a) Drawn curve: Specific heat of the alternating chain at $h=2.19$ (b) Dotted curve: Specific heat of the linear chain of effective spins with $J_{\parallel}/J_{\perp}=0.5$. (c) Dashed curve: Schottky anomaly due to the higher-energy levels of the spin pairs. (d) Dot-dashed curve: sum of curve (b) and (c).

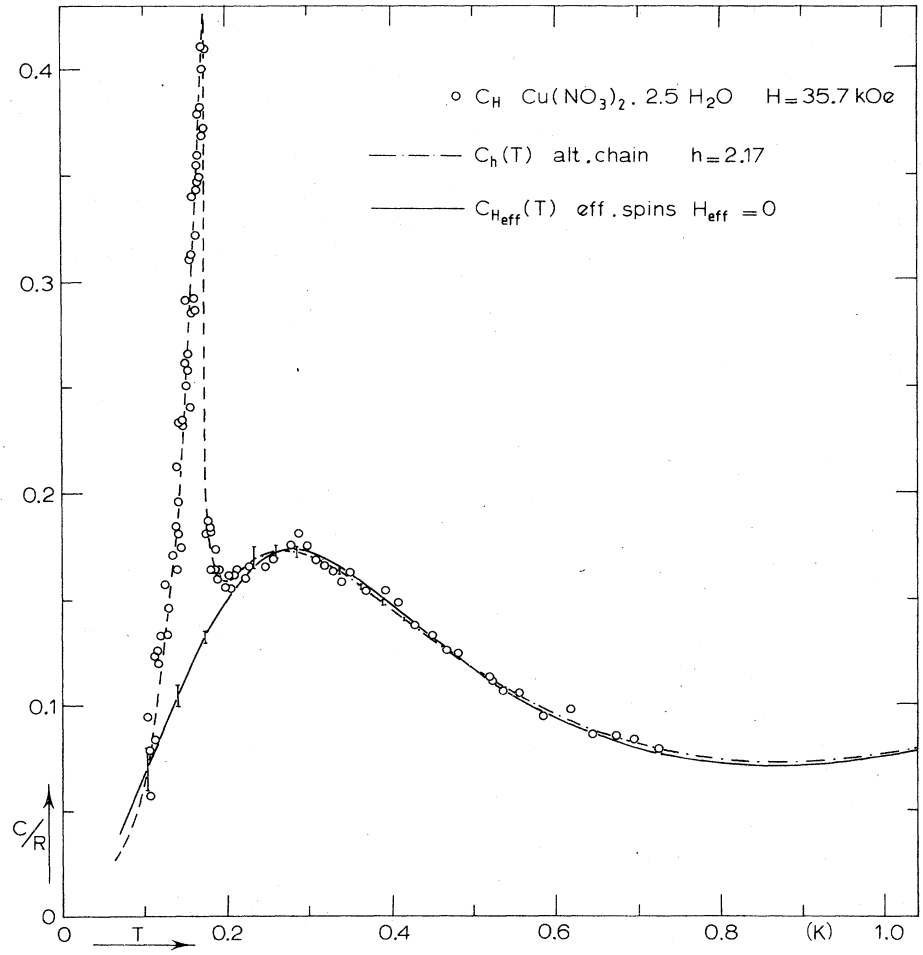

FIG. 7. Drawn curve and dot-dashed curve: Specific heat of the effective spins and of the alternating chain, respectively, as also given in Fig. 6. Dashed curve: Curve through the experimental data of $Cu(NO_3)_2 \cdot 0.5H_2O$ indicating the λ anomaly.

lated adiabatic and isothermal differential susceptibility, respectively, of the alternating Heisenberg AF chain for $g\mu_B H/|J| \equiv h = 2.25$ as a function of temperature. The experimental susceptibility data, obtained in relative units, were scaled at high temperatures to the theoretical adiabatic susceptibility. The error bars in Fig. 5 indicate the accuracy of the theoretical curve $\chi_{S,h}(T)$. The accuracy of the $\chi_{T,h}(T)$ curve is comparable to that of the $\chi_{S,h}(T)$ curve. The isothermal susceptibility clearly exceeds the adiabatic susceptibility at all temperatures but $T = 0$, at which $\chi_{S,h}(0) = \chi_{T,h}(0)$. The theoretical value of the susceptibility at $T = 0$ was obtained from the theoretical magnetization $M_0(H)$ curve which was discussed in Sec. V (Fig. 2).

The theoretical adiabatic differential susceptibility of the alternating Heisenberg AF chain and the experimental data on $Cu(NO_3)_2 \cdot 2.5H_2O$ agree nearly perfectly down to $T \approx 0.3$ K ($kT/|J| \approx 0.11$). Below this temperature down to the transition temperature to the long-range ordered state (indicated by T_N in Fig. 5), the experimental data lie just above the theoretical curve $\chi_{S,h}(T)$. The differences are, however, of the order of the accuracy of the theoretical curve. At T_N, the slope of the curve through the experimental data shows a discontinuity. Just below T_N, $\chi_{S,h}$ of $Cu(NO_3)_2 \cdot 2.5H_2O$ drops off quickly. At about $T = 0.1$ K it levels off to reach its zero-temperature value. We have discussed the behavior of $\chi_{S,h}(T)$ of $Cu(NO_3)_2 \cdot 2.5H_2O$ at and below T_N in more detail in Paper II.

IX. SPECIFIC HEAT AT $h = 2.17$

Calculated specific-heat data at $h = 2.17$ ($h \equiv g\mu_B H/|J|$ shows (Fig. 6) two maxima of about the same height; one at $kT/|J| = 1.2$ ($C/R = 0.189$), originating from the energy gap between the lowest-energy band and the excited ones, and the other at $kT/|J| = 0.105$ ($C/R = 0.173$), originating from the lowest-energy band itself. The entropy content of each anomaly is about $\frac{1}{2}R\ln 2$. In Fig. 7 are shown: (a) the low-temperature anomaly, (b) the curve obtained from the effective spin model (discussed later), and (c) the experimentally obtained specific heat of $Cu(NO_3)_2 \cdot 2.5H_2O$. The λ anomaly marks the transition to the 3D long-range-ordered state. Above the phase transition, the agreement between both theoretical curves and the experimental data is within the experimental accuracy. Because of the λ anomaly, the remaining entropy of $Cu(NO_3)_2 \cdot 2.5H_2O$ is removed more rapidly towards lower temperatures than according to the calculated curve. The entropy content below $T = 0.80$ K obtained from the measured $C_H(T)$ curve is about $\frac{1}{2}R\ln 2$.[24] The extrapolation of the specific heat of the finite clusters $n = 2, \ldots, 12$ to the specific heat of the infinite chain at the low-temperature side of the lowest anomaly becomes very inaccurate. This is indicated by the error bars in Figs. 6 and 7. We may, however, expect the specific heat, which is determined by the lowest continuous energy band if $h_{c1} < h < h_{c2}$, to be linearly dependent on T at low temperatures. Outside this anomalous region,

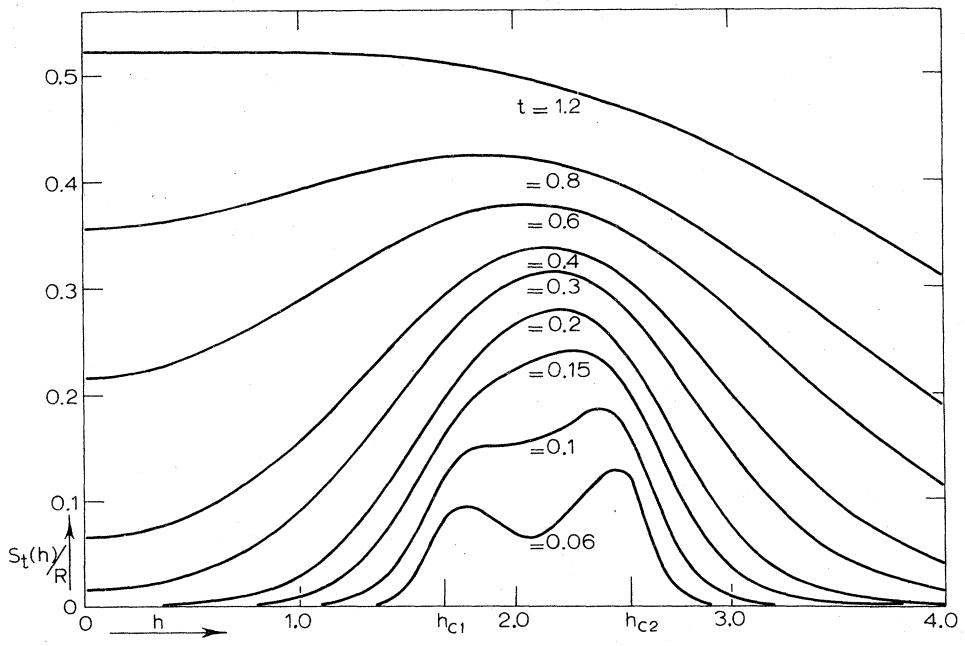

FIG. 8. Calculated entropy S/R of the alternating chain with $\alpha = 0.27$ at constant temperature vs the applied field.

there is an energy gap between the singlet ground state and the first excited states, which leads to an exponential temperature dependence for the low-temperature specific heat. Rigorous calculations on the isotropic X-Y alternating chain by Perk *et al.*[13] indeed lead to such dependences of $C_H(T)$. The low-temperature behavior of the experimentally obtained $C_H(T)$ curves at fields between h_{c1} and h_{c2} are determined by the λ anomaly. The measured $C_H(T)$ curves at fields outside the anomalous region indeed show an exponential dependence on T for low temperatures.[24]

X. ENTROPY AND ISENTROPES

From the energy-level scheme, it is clear that outside the anomalous region $h_{c1} - h_{c2}$ the entropy is removed at relatively high temperatures, because of the energy gap separating the singlet ground state and the higher levels. Between h_{c1} and h_{c2}, approximately $\frac{1}{2}R\ln 2$ of entropy, the amount contained in the acoustical band, has to be removed at lower temperatures. In Fig. 8, the entropy of the alternating chain ($\alpha = 0.27$) versus the external field is plotted for several tempera-

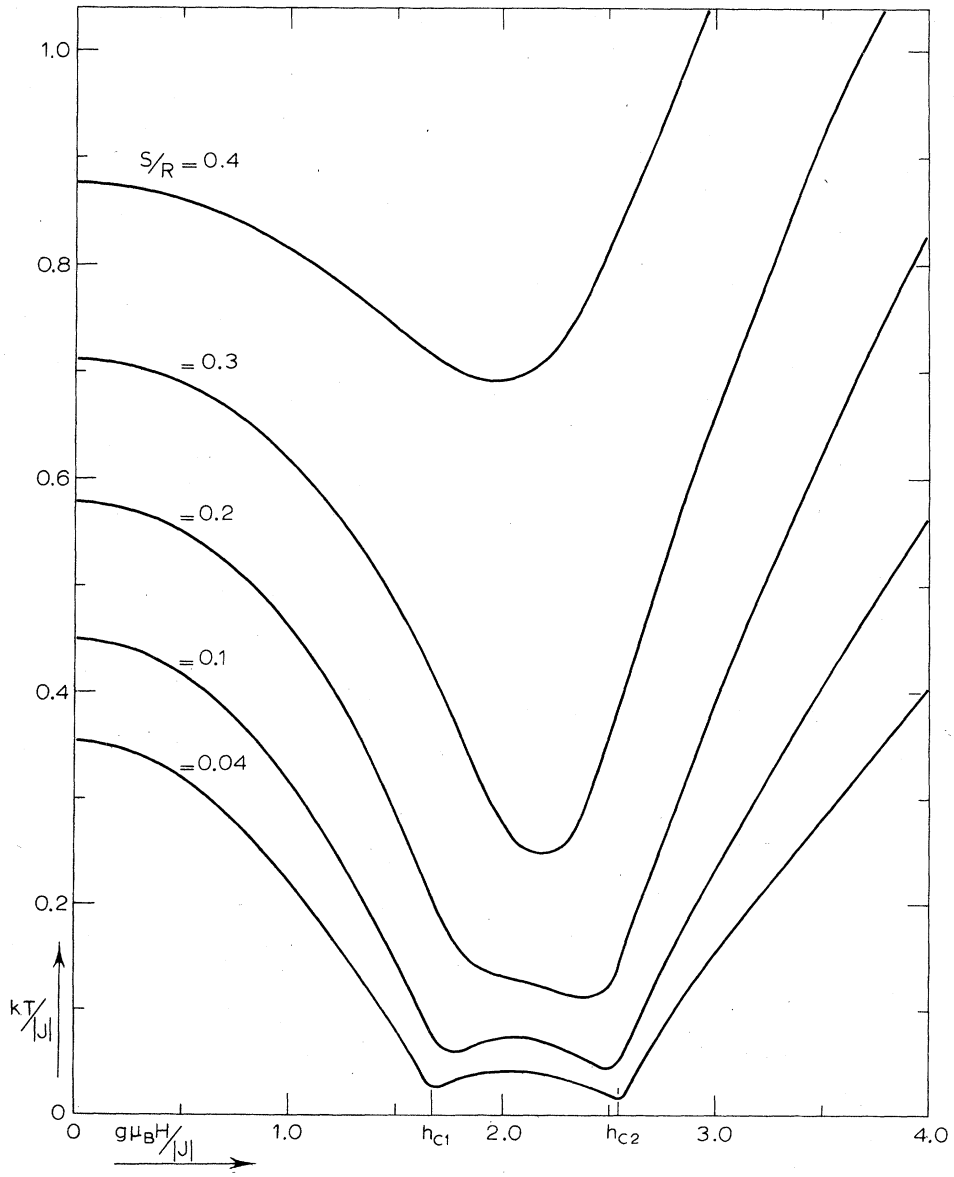

FIG. 9. Calculated cooling curves $T_S(H)$ of the alternating chain. The minima at the critical fields h_{c1} and h_{c2} are clearly different.

tures. Clearly, the entropy increases as a function of h towards the critical fields, while it is somewhat lower in between h_{c1} and h_{c2}. The calculated maximum of $S_T(H)$ at h_{c1} is lower than the maximum at h_{c2}. The field dependence of the entropy provides the opportunity of cooling adiabatically via a magnetization (demagnetization) procedure, from low (high) fields towards the critical fields. In Fig. 9, the calculated isentropes are drawn.

Haseda[38] first reported cooling experiments in $Cu(NO_3)_2 \cdot 2.5H_2O$ as described above. Later, Van Tol *et al.*[24] performed similar measurements in the anomalous region down to much lower temperatures. His results are shown in Fig. 10. Van Tol[24,27] attributed the differences in height of the two temperature minima at about h_{c1} and h_{c2} to strong anisotropy of the interaction J. Our experimental study (Papers I and II) showed, however, that J and $J'(\alpha J)$ are largely isotropic. The above discussed calculations of $T_S(H)$ resulting in Fig. 9 clearly prove that the asymmetry of $T_S(H)$ around $\frac{1}{2}(h_{c1}+h_{c2})$ is, in fact, a characteristic property of the alternating Heisenberg AF chain.

The qualitative agreement between Van Tol's experimentally obtained isentropes and our calculations is very good. Especially in the long-range-ordered state we expect a different dependence of S on its parameters than for an isolated alternating chain. At very low temperature, the heat capacity of the proton and Cu nuclear spins introduces additional discrepancies. The heat capacity of the nuclei increases towards lower temperatures and will certainly limit the lowest obtainable temperature in a cooling experiment.

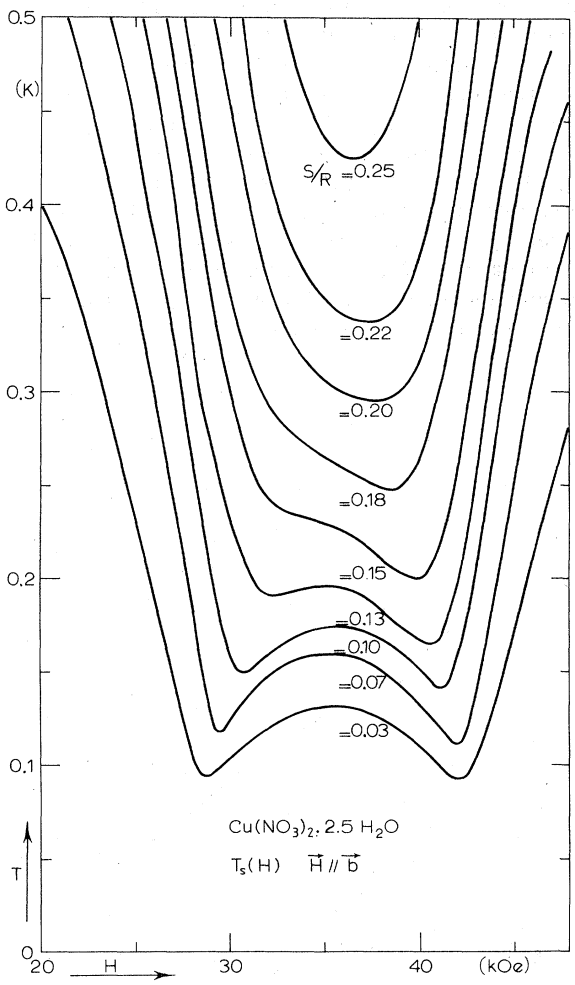

FIG. 10. Measured cooling curves $T_S(H)$ of $Cu(NO_3)_2 \cdot 2.5H_2O$ for $\vec{H} \parallel \vec{b}$.

XI. EFFECTIVE SPIN MODEL

In our previous papers on $Cu(NO_3)_2 \cdot 2.5H_2O$,[21,22] we have tried to describe the properties in the anomalous region on the basis of the effective spin $S=\frac{1}{2}$ formalism, introduced by Tachiki.[25] In Fig. 6, the calculated temperature dependence of the specific heat of the effective spins plus the Schottky anomaly due to the depopulation of the higher levels of the spin pair are compared to our present theoretical results. From Fig. 7, it is seen that the low-temperature anomaly calculated for the effective spin model fits the experimental data on $Cu(NO_3)_2 \cdot 2.5H_2O$ as accurate as the $C_H(T)$ curve of the alternating chain fits these data. The field dependences $\chi(H)$, $M(H)$, and $T_S(H)$ calculated on the basis of this effective spin model show, however, complete symmetry around $h_{1/2} = \frac{1}{2}(h_{c1}+h_{c2})$. This is clearly in contrast to our new calculations and our experimental results. The value of the critical field h_{c1} calculated on the basis of the effective spin model is also somewhat lower than the experimentally determined value. This leads to the conclusion that the effective spin model is inadequate to describe all features of the alternating $S=\frac{1}{2}$ chain in the anomalous region. We have compared the exactly calculated energy spectra of a number of alternating chains with those calculated on the basis of the effective spin formalism (a regular anisotropic chain with $J_\parallel/J_\perp=\frac{1}{2}$ of effective spins $S=\frac{1}{2}$). It appears that differences between the so-calculated energy levels are of the order of $J\alpha^2=J'\alpha$. The relative discrepancy in the width of the anomalous region introduced by the use of the effective spin formalism is consequently of the order of α. In the case of $Cu(NO_3)_2 \cdot 2.5H_2O$, where $\alpha=0.27$, this discrepancy is 10%. The effective spin formalism becomes "exact" in the limit of $\alpha \to 0$.

TABLE I. Exchange constants for $Cu(NO_3)_2 \cdot 2.5\ H_2O$. These values have been obtained experimentally (Papers I and II).

J/k	$=(-2.60 \pm 0.02)$K
$\alpha J/k$	$=(-0.70 \pm 0.05)$K
α	$= 0.27 \pm 0.02$
J_b''/k	$=(+0.05 \pm 0.03)$K
$J_{a\text{-}c}''/k$	$=(-0.05 \pm 0.03)$K

XII. DISCUSSION

In this paper, we have given several calculated thermodynamic properties of the Heisenberg alternating linear antiferromagnet applied particular to the case of $Cu(NO_3)_2 \cdot 2.5H_2O$; i.e., limited to the alternation ratio $\alpha = 0.27$. Comparison with the experimental data of $Cu(NO_3)_2 \cdot 2.5H_2O$ shows an excellent agreement, when the parameters listed in Table I are used. These parameters have been earlier obtained experimentally, as is described in Papers I and II. The properties of the AF Heisenberg alternating chain prove to be quite similar in many aspects to those of the isotropic AF X-Y alternating linear chain. This may justify the theoretical approach to study the alternating Heisenberg chain by considering the X-Y alternating chain and treating the longitudinal coupling by perturbative and decoupling methods.

From the crystal structure of $Cu(NO_3)_2 \cdot 2.5H_2O$ alone, it is not clear whether the AF spin pairs are coupled by the weaker 1D AF interactions (αJ) into spin ladders or into alternating chains (see Papers I and II for an extensive discussion on this problem). Also, the comparison of the experimental results with calculations using the effective formalism did not lead to a conclusive choice between the models. Finally, we managed to exclude the spin ladder as a result of a detailed experimental study of the spin configuration in the long-range-ordered state (Paper II). To see to what extent the calculated thermodynamic properties in the paramagnetic state could support this experimental conclusion, we have also calculated the thermodynamic properties of the spin ladder in a manner analogous to that presented here for the alternating chain. As one might have anticipated, only very small differences between the thermodynamic behavior of both models are seen in the case of small α. For $\alpha = 0.27$, characteristic properties, like the different behavior of $\chi(H)$ and $T_S(H)$ at the two critical fields, are analogous for both systems, and the difference of the extrapolated heat capacities of both systems (when significant) does not exceed the experimental accuracy. Evidently, the thermodynamic properties of a ladder and an alternating chain are very much the same for small α. Discrimination between them is therefore only possible from a study of microscopic properties.[22]

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[1] E. H. Lieb and D. C. Mattis, *Mathematical Physics in One Dimension; Exactly Soluble Models of Interacting Particles* (Academic, New York, 1966).
[2] L. J. de Jongh and A. R. Miedema, Adv. Phys. 23, 1 (1974).
[3] R. Lynden-Bell and H. M. McConnell, J. Chem. Phys. 37, 794 (1962).
[4] L. N. Bulaevskii, Sov. Phys. Solid State 13, 2778 (1972).
[5] P. L. Nordio, Z. G. Soos, and H. M. McConnell, Ann. Rev. Phys. Chem. 17, 237 (1966).
[6] W. Duffy Jr. and K. P. Barr, Phys. Rev. 165, 647 (1968).
[7] D. B. Abraham, J. Chem. Phys. 51, 2795 (1969).
[8] A. J. Silverstein and Z. G. Soos, J. Chem. Phys. 53, 326 (1970).
[9] M. Inoue and M. Kubo, J. Magn. Reson. 4, 175 (1971).
[10] E. J. Samuelson and M. Melamud, J. Phys. C 6, 3305 (1973).
[11] A. Brooks Harris, Phys. Rev. B 7, 3166 (1973).
[12] M. Takahashi, J. Phys. C 6, 2569 (1976).
[13] J. H. H. Perk, H. W. Capel, Th. J. Siskens, and M. J. Zuilhof, Physica (Utr.) A 81, 319 (1975).
[14] L. S. J. M. Henkens, K. M. Diederix, T. O. Klaassen, and N. J. Poulis, Physics (Utr.) B 83, 147 (1976).
[15] L. S. J. M. Henkens, M. W. van Tol, K. M. Diederix, T. O. Klaassen, and N. J. Poulis, Phys. Rev. Lett. 36, 1252 (1976).
[16] J. P. Groen, T. O. Klaassen, and N. J. Poulis, Phys. Lett. 62, 453 (1977).
[17] W. J. M. de Jonge, J. P. A. M. Hijmans, F. Boersma, J. C. Schouten, and K. Kopinga, Phys. Rev. Lett. (to be published).
[18] P. J. Kuindersma, Ph.D. thesis (University of Groningen, 1975) (unpublished).

[19]I. S. Jacobs, J. W. Bray, H. R. Hart Jr., L. V. Interrante, J. S. Kaspers, D. E. Prober, and J. C. Bonner, Phys. Rev. B 14, 3036 (1976).
[20]P. Pincus, Solid State Commun. 9, 1971 (1971).
[21]K. M. Diederix, J. P. Groen, J. S. J. M. Henkens, T. O. Klaassen, and N. J. Poulis, Physica (Utr.) B 93, 99 (1978).
[22]K. M. Diederix, J. P. Groen, L. S. J. M. Henkens, T. O. Klaassen, and N. J. Poulis, Physica (Utr.) B 94, 9 (1978).
[23]K. M. Diederix, J. P. Groen, and N. J. Poulis, Physica (Utr.) B86–B88, 1151 (1977).
[24]M. W. van Tol, K. M. Diederix, and N. J. Poulis, Physica (Utr.) 64, 363 (1973).
[25]M. Tachiki and T. Yamada, Prog. Theor. Phys. Suppl. 46, 291 (1970); and references therein.
[26]J. C. Bonner and M. E. Fisher, Phys. Rev. 135, A640 (1964).
[27]M. W. von Tol, Ph.D. thesis (University of Leiden, 1972) (unpublished).
[28]H. W. J. Blöte, Physica (Utr.) 78, 302 (1974); Physica (Utr.) B 79, 427 (1975); *ibid.* 93, 93 (1978).
[29]J. C. Bonner, S. A. Friedberg, H. Kobayashi, and B. E. Myers, in *Proceedings of the Twelfth International Conference on Low Temperatures Physics, Kyoto, Japan, 1970,* edited by E. Kanda (Keigaku, Tokyo, 1971), p. 691; and (unpublished).
[30]J. C. Bonner and S. A. Friedberg, Phase Trans 1973/ *Proceedings of the International Conference on Phase Transitions and Their Applications in Material Science,* edited by H. K. Henish, R. Roy, and L. E. Cross (Pergamon, New York, 1973), p. 429.
[31]K. M. Diederix, H. A. Algra, J. P. Groen, T. O. Klaassen, N. J. Poulis, and R. L. Carlin, Phys. Lett. A 60, 247 (1977).
[32]S. A. Friedberg and C. A. Raquet, J. Appl. Phys. 39, 1132 (1968).
[33]L. S. J. M. Henkens, K. M. Diederix, T. O. Klaassen, and N. J. Poulis, Physics (Utr.) B 81, 259 (1976).
[34]R. B. Griffiths, Phys. Rev. 133, A768 (1964).
[35]M. Drawid and J. W. Halley, AIP Conf. Proc. 34, 208 (1976).
[36]J. C. Bonner and H. W. J. Blöte (unpublished).
[37]M. W. van Tol, H. M. C. Eijkelhof, and A. J. van Duyneveldt, Physica (Utr.) 60, 223 (1972).
[38]T. Haseda, Y. Tokunaga, R. Yamada, Y. Kuramitsu, S. Sakatsuma, and K. Kamaya, *Proceedings of the Twelfth International Conference on Low Temperatures Physics, Kyoto, Japan, 1970,* edited by E. Kanda (Keigaku, Tokyo, 1971), p. 685.
[39]J. A. Osborn, Phys. Rev. 67, 35 (1945).