

MAGNETIC HEAT CAPACITY OF ANTIFERROMAGNETIC Co, Ni, Mn, AND Fe CARBONATES

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The heat capacities of CoCO_3 , NiCO_3 , MnCO_3 , FeCO_3 , and CaCO_3 are measured in the temperature range 1.6–70°K. For the first four of these compounds the maximum heat capacity is observed at 17.0, 22.2, 29.4, and 30.6°K, respectively, and is associated with the antiferromagnetic transition. The data for CaCO_3 are used to calculate the lattice heat capacity and to determine the magnetic heat capacity of magnetic carbonates. The entropy of ion magnetic moment ordering is computed. At helium temperatures the magnetic heat capacity obeys the law $C_M = aT^3$ according to spin-wave theory. The values of the constant a for Co, Ni, and Mn carbonates (13.5 , 15.3 , and 18.0×10^{-4} joule/deg⁴-mole, respectively) are from 10 to 20 times larger than the corresponding constants for the lattice heat capacity and agree with the values calculated from magnetic measurements. Excitation of the second branch of the spin-wave spectrum is observed at temperatures close to $T_N/10$ for MnCO_3 and $T_N/3$ for CoCO_3 and NiCO_3 .

1. INTRODUCTION

THE existing spin-wave theory of antiferromagnets has hitherto not been supported by sufficiently reliable experimental evidence. The investigation of the temperature dependence of heat capacity at low temperatures is important as a means of studying the spin-wave spectra. In the case of antiferromagnets this method encounters two difficulties. First, the condition $T_N \ll \Theta_D$ must be fulfilled to permit a confident separation of the magnetic heat capacity from the lattice heat capacity. On the other hand, T_N must not be too small if the condition $T \ll T_N$ is to be satisfied in the attainable temperature region (desirably at liquid helium temperatures). The optimum values of T_N are ~ 20 – 40°K . Second, the existence of a considerable energy gap in the spin-wave spectrum of most antiferromagnets results in the fact that at very low temperatures ($T \ll T_N$) their magnetic heat capacity must vary exponentially; it is practically impossible to observe this behavior experimentally. The second difficulty disappears when we investigate uniaxial antiferromagnets having the antiferromagnetic vector perpendicular to the axis. These include the rhombohedral carbonates of Mn, Co, and Ni, in which the magnetization of sublattices has a considerable component perpendicular to the axis.^[1-3] Borovik-Romanov^[1] and Turov^[4] have investigated the spin-wave spectra

of such compounds and have shown that two branches exist. The lower branch, corresponding to spin oscillations in the basal plane, exhibits practically no gap and is a pure phonon spectrum making a contribution $C_1 = aT^3$ to the heat capacity. This agrees with the temperature dependence of the lattice heat capacity; however, because of the small value of T_N the magnetic heat capacity must be one order of magnitude greater than the lattice heat capacity and thus can easily be separated from the total heat capacity. The second branch has the usual antiferromagnetic gap $kT_{AE} = \mu\sqrt{H_A H_E}$ (H_A is the anisotropy field and H_E is the effective field of exchange energy) and should not contribute to the heat capacity at low temperatures. At $T \sim T_{AE}$ the oscillations of this branch begin to be excited appreciably. This should lead to a sharp rise of the heat capacity; therefore for $T > T_{AE}$ the heat capacity should again obey a cubic law with doubling of the coefficient ($C_1 + C_2 = 2aT^3$).

An important advantage was derived from the fact that the given carbonates were antiferromagnets possessing weak ferromagnetism. From magnetic measurements we know the temperature dependence of their spontaneous magnetic moment σ , which in agreement with spin-wave theory has the form

$$\sigma/\sigma_0 = 1 - \eta(T/T_N)^2.$$

The relation between the coefficients α and η has been investigated in [1] and [4]. The measurement of heat capacities has thus led to the possibility of verifying the spin-wave theory quantitatively. In distinction from the aforementioned three carbonates, in FeCO_3 the spins are parallel to the principal axis, [3,5] so that the magnetic heat capacity should be practically nonexistent at low temperatures.

In order to provide a possibility of separating the magnetic heat capacity from the lattice heat capacity we measured the heat capacity of the isomorphous nonmagnetic compound CaCO_3 . For this purpose the heat capacities of all the carbonates were investigated up to temperatures considerably above T_N .

It has been shown in a preliminary report [6] that the foregoing discussion is confirmed by heat capacity measurements on MnCO_3 . In the present work we give more detailed data for MnCO_3 as well as for all the aforementioned carbonates. The results are discussed on the basis of the foregoing theoretical ideas.

2. SAMPLES AND MEASUREMENT TECHNIQUE

The CaCO_3 sample was a transparent natural single crystal of feldspar cut in the form of a cylinder of 30-mm diameter and containing 1.3 moles. The FeCO_3 sample was 97%-pure natural siderite¹⁾ cut in the form of a cylinder of 27-mm diameter and containing 1.3 moles. The MnCO_3 sample in the form of small crystals (of average linear dimension ~ 0.3 mm) was prepared hydrothermally in the Institute of Crystallography of the U.S.S.R. Academy of Sciences. [7] ²⁾ The total weight of these crystals was ~ 0.13 mole. The fine-crystalline NiCO_3 sample (particles of linear dimension ~ 0.2 mm) was also prepared hydrothermally in the Institute for Physical Problems³⁾ and contained ~ 0.4 mole. At the same institute 0.3 mole of fine-crystalline CoCO_3 (~ 0.05 -mm particles) was prepared. The purity of the samples was determined from the purity of the raw materials. In preparing NiCO_3 and CoCO_3 analytically pure raw materials were used.

¹⁾We are indebted to the staff of the Mineralogical Museum of the U.S.S.R. Academy of Science for assistance in selecting the sample.

²⁾The author is indebted to N. Yu. Ikomikova for providing the MnCO_3 crystals.

³⁾We wish to thank N. N. Mikhaïlov and Yu. F. Orekhov for performing the careful and tedious work of preparing the NiCO_3 and CoCO_3 crystals.

In the temperature range 1.6–20°K heat capacities were measured in a vacuum calorimeter; [8] in the 12–70°K range an adiabatic vacuum calorimeter was used. [9] The sample, either in the form of a single block or as small crystals held in a thin-walled container, was suspended from nylon threads within a vacuum can. In the first case an insulated manganese heating coil was wound directly around the sample and was cemented in place with BF-2 adhesive, for which the requisite heat capacity correction was made. [10] According to a calculation in [11] the heat capacity of the copper container was 1–2% of the total heat capacity in the range 1.6–20°K. In the adiabatic calorimeter the heat capacity of the empty container was measured directly. A small quantity of helium gas served to improve heat exchange between the crystals and the container. A computation showed that the head of adsorption of the gaseous heat-exchanger did not introduce more than a 3% error in heat capacity determinations even when the gas was completely adsorbed.

For temperature measurements in the 1.5–4°K region a phosphor-bronze resistance thermometer mounted on a copper disk was cemented to the end-face of the sample; in the interval 4–20°K a miniature carbon thermometer was used. [12] Temperatures in the range 12–70°K were measured with a platinum resistance thermometer placed in the center of the sample block or container.

Below 4°K the thermometers were calibrated according to the vapor pressure of liquid helium in degrees of the 1958 temperature scale. For the intermediate range 4–20°K the carbon thermometer was calibrated at three points—the normal boiling point of helium, the triple point of hydrogen, and the normal boiling point of hydrogen. [13]

The total error of the heat capacity measurements did not exceed 2–3% below 12°K and was not greater than 0.5% above 12°K.

3. EXPERIMENTAL RESULTS

The heat capacities of CoCO_3 , NiCO_3 , MnCO_3 , and FeCO_3 were measured in the range 1.6–70°K. The results, shown in Fig. 1, exhibit the characteristic maxima of heat capacities corresponding to transitions from the antiferromagnetic to the paramagnetic state. Maxima were observed at 17.0, 22.2, 29.4, and 30.6°K, respectively. The peaks had different widths and shapes, the sharpest peak being observed for CoCO_3 . In computing the entropy corresponding to antiferromagnetic ordering of the spins of Co^{++} , Ni^{++} , Mn^{++} , and Fe^{++} it was necessary to extrapolate the lattice heat capacity

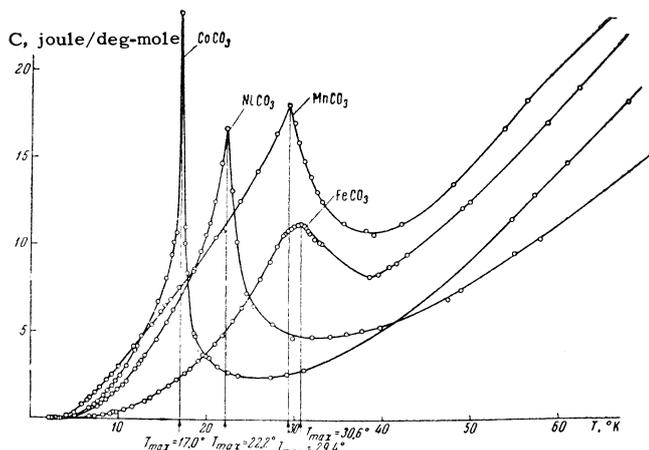


FIG. 1. Temperature dependence of molar heat capacity.

to lower temperatures. The heat capacities of all the carbonates behaved differently above the transition point; this is apparently associated with different Debye temperatures.

In order to devise a procedure for extrapolating the lattice heat capacity C_{lat} we measured the heat capacity of nonmagnetic CaCO_3 specially (Fig. 2). If we assume that the metal ion and the CO_3 ion vibrating together possess six degrees of freedom we can take $C_{lat} = 2D(\Theta_D/T)$, where D is the Debye function. Below 20°K the heat capacity obeys the simple cubic temperature law $C = 1.85 \times 10^{-4}T^3$ joule/deg-mole, from which we obtain $\Theta_D = 275^\circ\text{K}$. Figure 2 shows that the experimental heat capacity curve of CaCO_3 up to 60°K is well represented by

$$C = 2D(275/T). \quad (1)$$

At higher temperatures the experimental curve begins to turn upward. The known frequencies of internal vibrations in the CO_3 ion^[16] are too high and they make a negligible contribution to the heat capacity below 80°K . The extra growth of the heat

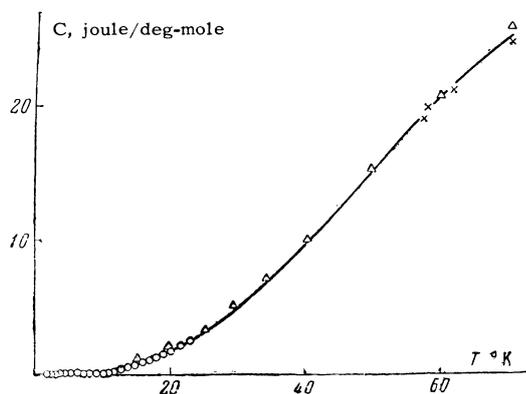


FIG. 2. Temperature dependence of the molar heat capacity of CaCO_3 . O — our measurements, Δ — Simon and Swain,^[14] x — Anderson.^[15] The continuous curve represents $C = 2D(275/T)$.

capacity evidently results from the excitation of rotational oscillations of CO_3 . Good agreement with experiment is obtained if the Einstein function $E(570/T)$ is added to (1). By analogy with CaCO_3 we obtain empirical equations describing the behavior of the lattice heat capacity from the transition temperature to 70°K :

$$\text{MnCO}_3: C_{lat} = 2D(281/T) + E(567/T), \quad (2)$$

$$\text{NiCO}_3: C_{lat} = 2D(386/T), \quad (3)$$

$$\text{CoCO}_3: C_{lat} = 2D(354/T) + E(448/T), \quad (4)$$

$$\text{FeCO}_3: C_{lat} = 2D(305/T) + E(525/T). \quad (5)$$

For all compounds the Einstein term corrections did not exceed 2% of the total heat capacity.

The lattice heat capacity estimated as described above can be assumed to differ from the true value by not more than 10–15%. The possible error in C_{lat} is most likely to be positive and is associated mainly with the uncertain termination of magnetic ordering. Therefore our calculations, based on the magnetic heat capacity ($C_M = C_{meas} - C_{lat}$), of the entropy (Table I) associated with antiferromagnetic ordering of Mn^{++} , Fe^{++} , Co^{++} , and Ni^{++} spins could be somewhat too low. It was found that approximately one-third of the magnetic entropy corresponds to temperatures above that of the heat capacity peak; this has been observed previously.^[17]

It is known^[18,19] that in transition metals and their salts the ordering of nuclear spins begins at liquid helium temperatures and that the corresponding additional contribution to the heat capacity is of the form $C_{nucl} = b/T^2$. We observed this term for MnCO_3 and CoCO_3 , which have non-zero nuclear magnetic moments. Figure 3 shows that for MnCO_3 we have $b = (2.7 \pm 0.5) \times 10^{-2}$ joule-deg/mole, which agrees within measurement error with the value of b for MnF_2 ,^[18] but is only one-half of the value for manganese fluosilicate and only one-fourth of the value for manganous ammonium sulfate.^[20] For CoCO_3 we obtained $b = (0.4 \pm 0.2) \times 10^{-2}$ joule-deg/mole, which is closer to the value for antiferromagnetic CoF_2 ^[21] and for metallic cobalt^[19] than for dilute salts. However, the ratio of values of b for the corresponding cobalt salts is

Table I

Compound	S_M , joule/ deg-mole	$(2s + 1)$, for free ion	$R \ln(2s+1)$, joule/ deg-mole
MnCO_3	14.43	6	14.89
FeCO_3	5.75	5	13.37
CoCO_3	5.75	4	11.51
NiCO_3	8.91	3	9.12
—	—	2	5.76

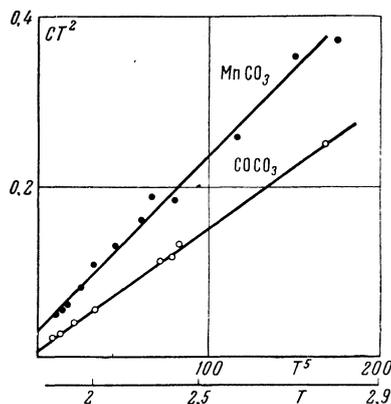


FIG. 3. CT^2 as a function of T^5 in the region where nuclear heat capacity is exhibited.

approximately the same as for manganese salts.^[19]

Nuclear heat capacity has not been observed experimentally in FeCO_3 and NiCO_3 ; this agrees with the fact that Fe and Ni have zero magnetic moments.

By calculating separately the lattice and nuclear heat capacities in the above-described manner, we obtained the temperature dependence of the magnetic heat capacity.

4. DISCUSSION OF RESULTS

The temperature of the transition to the antiferromagnetic state of CoCO_3 , which we determined from the heat capacity maximum, is 17.0°K ; this is 1.1°K below the temperature $T_N = 18.1^\circ\text{K}$ obtained from magnetic data.^[2] For MnCO_3 the maximum at 29.4°K is also 3°K below the point $T_N = 32.4^\circ\text{K}$ obtained from magnetic measurements.^[1] For NiCO_3 we obtained $T_{\text{max}} = 22.2^\circ\text{K}$ and for FeCO_3 we obtained $T_{\text{max}} = 30.6^\circ\text{K}$. Reliable magnetic data for these materials are still not available. A similar discrepancy in the transition temperatures was observed previously for the fluorides MnF_2 , FeF_2 , and CoF_2 ,^[22,23] with the value of T_N obtained from magnetic measurements always higher and with the discrepancy apparently exceeding the measurement error.

Figure 4 shows the dependence of the heat capacity on the relative temperature near T_N . It is quite clear that in the given coordinates the widths of peaks also differ greatly even among similar antiferromagnetic compounds. The sharpest and narrowest peak is observed for CoCO_3 and the broadest peak is observed for MnCO_3 .

Table I gives the magnetic entropy S_M calculated for all of the investigated materials. In the cases of MnCO_3 and NiCO_3 the values of $S_M = R \ln(2s + 1)$ are consistent with the ground states of these ions, which are ${}^6S_{5/2}$ for Mn^{++} and 3F_4 for Ni^{++} . For CoCO_3 we found double degeneracy of the ion ground state in the crystalline

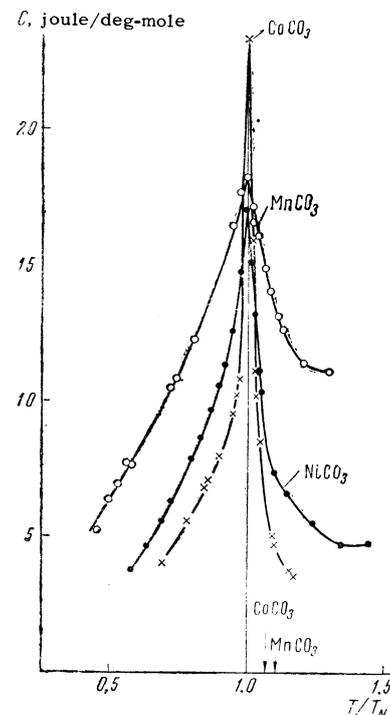


FIG. 4. Heat capacity as a function of T/T_N near the transition temperature. Arrows indicate the Néel temperature obtained from magnetic measurements.^[1,2]

field, although the ground term is ${}^4F_{9/2}$. Double degeneracy of CoF_2 was determined from the entropy.^[22]

The fact that the ground state of Co^{++} in the CoCO_3 lattice is a spin doublet is associated with the known splitting of the free ion term by the crystalline field and spin-orbit interaction.^[24] A similar result was obtained in the case of Fe^{++} . For the free ion the ground state is 5D_4 , and magnetic data for many Fe compounds agree with the hypothesis that the lowest level of Fe^{++} in the crystalline field is an orbital singlet with spin $s = 2$. Our results show that anomalous splitting also occurs in FeCO_3 ; this is confirmed by the anomalous increase in the susceptibility anisotropy of FeCO_3 at lower temperatures.^[5] This increase is similar to that observed in Co^{++} compounds.

As already mentioned, according to the spin-wave theory the magnetic heat capacity of the investigated carbonates should obey a cubic law for $T \rightarrow 0^\circ\text{K}$. Figure 5 shows the magnetic heat capacity data represented in the coordinates C_M/T and T^2 . Indeed, at sufficiently low temperatures $C_M \sim T^3$ is observed for all antiferromagnetic carbonates.

This qualitative confirmation of the theory has been checked quantitatively. The spin-wave theory gives for the magnetic heat capacity of Mn, Ni, and Co carbonates the temperature dependence

$$C_M = \frac{16\pi^2 k^2 \chi_{\perp}^0 T_N}{5g^2 \mu_B^2} \eta \left(\frac{T}{T_N} \right)^3 = aT^3. \quad (6)$$

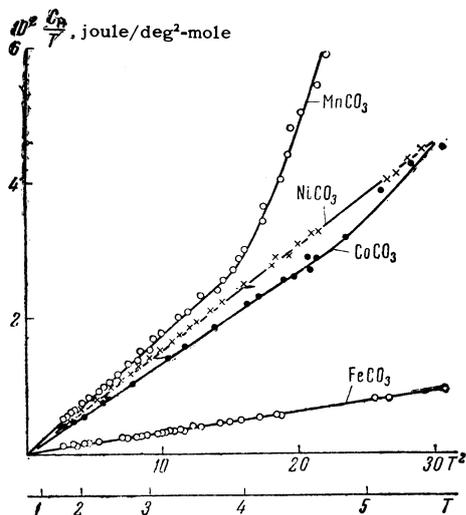


FIG. 5. Temperature dependence of magnetic heat capacity represented in the coordinates C_M/T and T^2 .

The constants χ_{\perp}^0 , g , and T_N were previously determined from magnetic measurements.^[1,2,25] The quantity η appears in the expression for the temperature dependence of weak ferromagnetism:

$$\sigma = \sigma_0 [1 - \eta (T/T_N)^2]$$

and was also determined from magnetic measurements on $MnCO_3$ ^[1] and $CoCO_3$.^[2]

The heat capacities and magnetic measurements are summarized in Table II, where the last column gives the values of η calculated from (6) on the basis of our heat capacity data.

The comparison has been most successful in the case of $MnCO_3$,^[6] for which all quantities in (6) have been determined with sufficient reliability. The table shows that the values determined from magnetic data agree fully with those calculated from (6).

In the case of $CoCO_3$ we do not possess reliable data on the g -factor; magnetic susceptibility data cannot be used for its determination because of the complicated level splitting. Paramagnetic resonance has not been observed in $CoCO_3$. We have estimated the g -factor very roughly using antiferromagnetic resonance data.^[26] Assuming the validity of the relation

$$(\nu/\gamma)^2 = (g^2/4)H_0(H_0 + H_D)$$

(where H_0 is the resonance field and H_D is the Dzyaloshinskii field) and using the value $H_0 = 0.1$ kOe we obtained $g = 4$ for $\nu = 9.6$ kMc and $H_D = 27$ kOe.

It is thus found that η_M and η_{calc} differ by 20%. Considering that the g factor was estimated only roughly, and that the theoretical calculation was not performed for the case of strong anisotropy, this agreement must be regarded as satisfactory.

For $NiCO_3$ experimental values of η_M are not available. Using magnetic measurements^[25] and heat capacity data, we calculated the value $\eta = 0.1$, which agrees in order of magnitude with the experimental values for $MnCO_3$ and $CoCO_3$.

For $FeCO_3$ we obtained a small magnetic term in the heat capacity which is not predicted by spin-wave theory. It is unlikely that this term resulted from incorrect extrapolation of the lattice heat capacity. The most likely explanation is insufficient purity of the sample (the natural mineral). Impurities and internal stresses cause weak ferromagnetism (specifically, the piezomagnetic effect).^[27] The presence of this weak ferromagnetism indicates that the antiferromagnetic vector does not lie exactly along the z axis, but has a component in the basal plane, which can introduce a small magnetic term proportional to T^3 in the heat capacity.

Figure 6 shows C_M/aT^3 as a function of T/T_N up to $T = T_N$. Following a region where $C_M/aT^3 = 1$ holds identically for all the investigated materials, the heat capacity begins to show a pronounced increase, which apparently results from the excitation of the second branch of the spin-wave spectrum having a $\sim kTAE$ gap.

The second branch begins to appear earliest for $MnCO_3$ (at $T/T_N \sim 0.13$). For $CoCO_3$ this occurs at $T/T_N \sim 0.29$, and for $NiCO_3$ at $T/T_N \sim 0.36$. According to the theory, when $T \gg T_{AE}$ the heat capacity should also obey a cubic law with doubling of the coefficient a at lower temperatures. This is actually observed in $MnCO_3$. In $CoCO_3$ the heat capacity of the second branch is 40% of that of the first branch; this can be associated with anisotropy of the g -factor [see Eq. (6)]. Similar excitation of both branches of the spin-wave spectrum has been

Table II

Compound	$10^4 C_{lat}/T^3$, joule/ deg ³ -mole	$10^4 C_M/T^3$, joule/ deg ³ -mole	χ_{\perp}^0	g	η_M	η_{calc}
$MnCO_3$	1.8	18.0	$43 \cdot 10^{-3}$	2	0.24	0.25
$NiCO_3$	0.7	15.3	$49 \cdot 10^{-3}$	2.1	—	0.1
$CoCO_3$	0.9	13.5	$53 \cdot 10^{-3}$	4	0.14	0.18
$FeCO_3$	1.4	3.2				

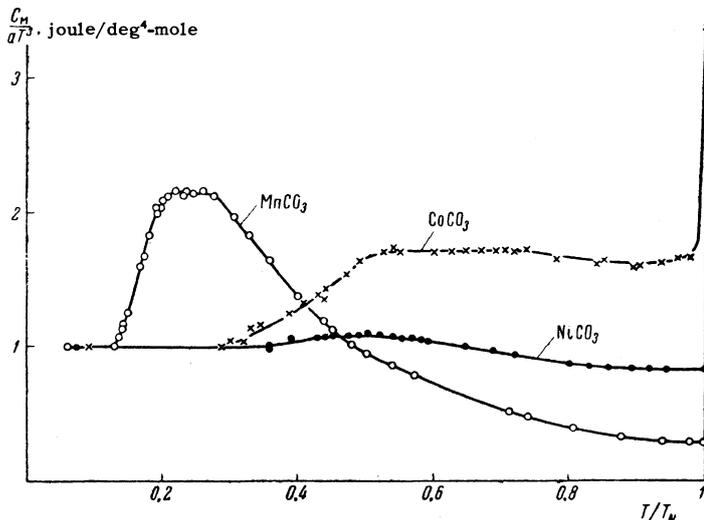


FIG. 6. Temperature dependence of magnetic heat capacity up to the transition temperature.

observed in the temperature dependence of spontaneous magnetization.^[2]

In the case of NiCO_3 the spin-wave theory apparently becomes inapplicable before full excitation of the second branch occurs. Figure 6 shows up to what temperatures the spin-wave theory can be applied. Departures from the power laws occur in the temperature regions above $0.3 T_N$. At the temperature when a sharp rise of the heat capacity, associated with excitation of the second branch, begins to appear we can estimate roughly the gap in this branch. Our results for T_{AE} were $\sim 15^\circ\text{K}$ for MnCO_3 , $\sim 32^\circ\text{K}$ for NiCO_3 , and $\sim 22^\circ\text{K}$ for CoCO_3 . We thus find that for the given materials the gap is of the order of T_N . It must be noted that the observed high-temperature power laws for CoCO_3 and MnCO_3 lie in the region $T < T_{AE}$. The theory permits rigorously only the case $T \gg T_{AE}$ for this branch, in disagreement with experiment.

In the case of FeCO_3 we were unable to observe an increase of the heat capacity corresponding to spin-wave excitation above the gap.

CONCLUSION

The following principal conclusions follow from our work.

1. From the entropy of ordering it follows that for Co^{++} and Fe^{++} ions in the investigated carbonates the crystalline field splits the ground state so that the lowest level is a simple spin doublet. For Mn^{++} and Ni^{++} , in accordance with the free-ion terms ${}^6S_{5/2}$ and 3F_4 , the lowest levels are $s = 5/2$ and $s = 1$.

2. Qualitative confirmation has been obtained for the predictions of spin-wave theory that in carbonates of Mn, Co, and Ni at low temperatures the phonon branch of spin waves is excited and that the corresponding magnetic heat capacity is proportional to T^3 . In the case of FeCO_3 , where this branch should not be excited, the magnetic heat capacity was found to be one order of magnitude smaller.

3. A comparison of the coefficients a obtained from heat capacity data with magnetic measurements on MnCO_3 and CoCO_3 confirmed the quantitative correctness of spin-wave theory for antiferromagnets.

4. Excitation of the second branch of the spin-wave spectrum was observed in all three carbonates.

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