

## Magnetic Properties of Cobalt and Manganese Carbonates

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The magnetic properties of  $\text{MnCO}_3$  and  $\text{CoCO}_3$  have been investigated in the temperature range 14 to 300° K. It was discovered that below  $T_c$  ( $T_c = 31.5^\circ$  K for  $\text{MnCO}_3$ ;  $T_c = 17.5^\circ$  K for  $\text{CoCO}_3$ ) the magnetic susceptibility increases abruptly and varies greatly with the field. To explain the observed anomalies, it is postulated that below  $T_c$  the carbonates go over to an antiferromagnetic state in which the moments of the sublattices do not fully compensate each other.

**B**IZETTE<sup>1</sup> discovered antiferromagnetism in siderite containing 78%  $\text{FeCO}_3$ . It seemed of interest to investigate the magnetic properties of other carbonates of elements of the iron group. We have investigated the temperature variation of the magnetic susceptibility of  $\text{MnCO}_3$  and of an anhydrous sample of  $\text{CoCO}_3$  in the range 14 to 300° K.

The magnetic properties of manganese carbonate were studied on three specimens. The first specimen used was a commercial sample of "ch.d.a." brand; it was not subjected to drying, because we feared partial dissociation upon drying. The second specimen was the same sample subjected to drying at 160° C, in an ampoule hermetically joined to a vessel containing an absorber ( $\text{CaCl}_2$ ). Finally, for the manufacture of the third specimen we used a sample we ourselves had prepared. This sample was obtained by heating for 20 hours at 160° C, in a closed test tube, a mixture of a saturated solution of  $\text{MnCl}_2$  with  $\text{CaCO}_3$ .<sup>2</sup> The values of susceptibility obtained for the first and third specimens lay systematically lower (by 15 and 18%); this was caused by the presence of sorbed water in the first specimen and of residues of  $\text{CaCO}_3$  in the third. After introduction of correc-

tions according to weight, the susceptibility values of all three specimens agreed over the whole temperature range within the limits of experimental error.

Two specimens of anhydrous  $\text{CoCO}_3$  were investigated. We obtained them by the same method as the  $\text{MnCO}_3$ —by heating, in a closed ampoule, a mixture of a saturated solution of  $\text{CoCl}_2$  with  $\text{CaCO}_3$ . The results obtained for the two samples likewise agreed, within the limits of experimental error, after correction according to weight (13%).

The susceptibility measurements were made by the Faraday method, on apparatus similar to that developed earlier<sup>3</sup>. This apparatus permitted continuous coverage of the wide range of temperatures from 14 to 300° K. The accuracy of the temperature measurement was not worse than  $\pm 0.5^\circ$  at hydrogen temperatures, and better than  $\pm 0.1^\circ$  at higher temperatures. The error in the absolute measurement of susceptibility was not greater than 5%; in the relative measurement, less than  $\pm 2\%$ .

The temperature variation of the magnetic susceptibility of both carbonates at high temperatures satisfied the Curie-Weiss law  $\chi_m = C_M / (T + \Theta)$ . The values of the constants  $C_M$  and  $\Theta$  are given in the table.

TABLE

Compound	Range of validity of Curie-Weiss law	$C_M$	$\Theta$	$\chi_{\text{eff}}$		$T_c$ °K
				Theor.	Exptl.	
$\text{MnCO}_3$ . .	75—300°K	4.78	64.5	5.92	6.26	31.5
$\text{CoCO}_3$ . .	50—300°K	1.24	65	3.87	4.34	17.5

In the same Table are given the values of  $\mu_{\text{eff}}$  calculated from our measurements of  $C_M$ , and the theoretical values of  $\mu_{\text{eff}}$  calculated on the assumption of complete "quenching" of the orbital moments.<sup>4</sup> The results of the susceptibility measurement below 100° K are given in Fig. 1 for  $\text{MnCO}_3$  and in Fig. 2 for  $\text{CoCO}_3$ .

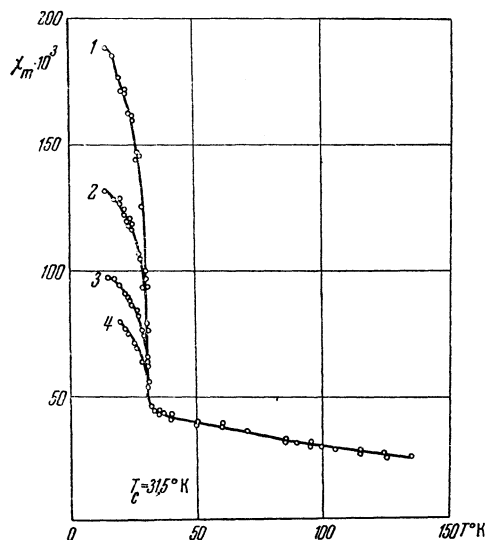


FIG. 1. Temperature dependence of the molar magnetic susceptibility  $\chi_m$  of manganese carbonate: 1 -  $H = 490$  oersteds; 2 -  $H = 920$  oersteds; 3 -  $H = 1790$  oersteds; 4 -  $H = 2650$  oersteds.

Below some critical temperature  $T_c$ , the susceptibility increases abruptly and exhibits a strong dependence on the field. Also observed is a slight hysteresis, which we did not investigate in detail. Figure 3 shows the dependence of the magnetic moment  $M$  on the field intensity  $H$  for manganese carbonate at temperatures 15 to 40° K. We see that at temperatures below  $T_c$  (for fields above about 600 oe), this variation can be represented as the sum of two terms,  $M = M_0 + \chi' H$ . Similar isotherms were obtained for  $\text{CoCO}_3$ . A field dependence of this type was also observed earlier on a series of other compounds,<sup>5,6</sup> but so far no complete explanation has been found.

From the plotted isotherms  $M(H)$ , we determined the temperature dependence of  $M_0$  for  $\text{MnCO}_3$  (Fig. 4) and for  $\text{CoCO}_3$  (Fig. 5). It has the form characteristic of an ordering curve. For  $T \rightarrow 0$ , however,  $M_0$  approaches a value considerably smaller than the value of magnetic moment to be expected at ferromagnetic saturation ( $M_{\text{fer}} = N\beta\mu_{\text{eff}}$ ).

For  $\text{MnCO}_3$ :  $M_0 = 68$ ,  $M_{\text{fer}} = 32000$ .

For  $\text{CoCO}_3$ :  $M_0 = 400$  to 1000,  $M_{\text{fer}} = 27200$ .

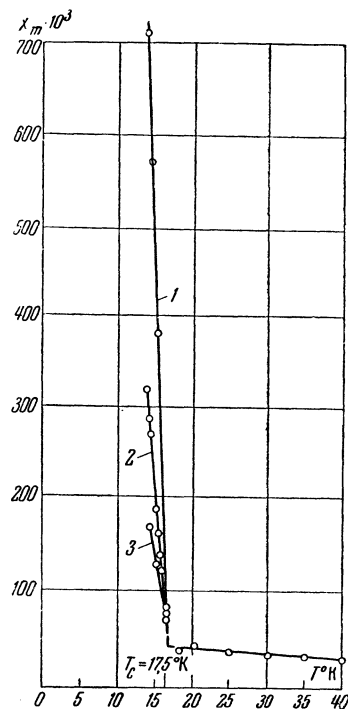


FIG. 2. Temperature dependence of the molar magnetic susceptibility  $\chi_m$  of cobalt carbonate: 1 -  $H = 490$  oersteds; 2 -  $H = 1790$  oersteds; 3 -  $H = 2650$  oersteds.

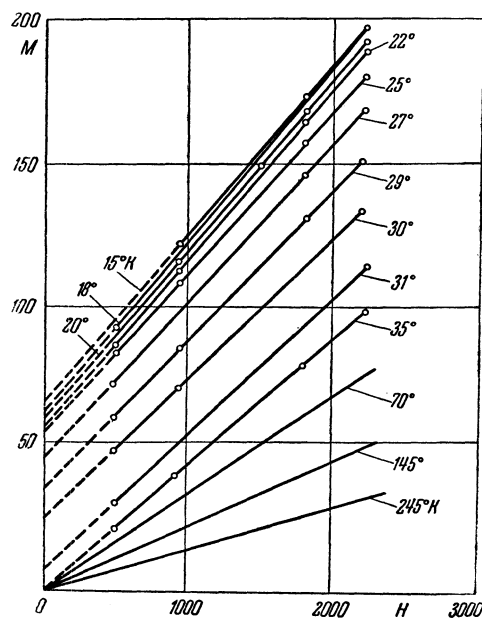


FIG. 3. Dependence of the magnetic moment  $M$  on field  $H$  at various temperatures, for  $\text{MnCO}_3$ .

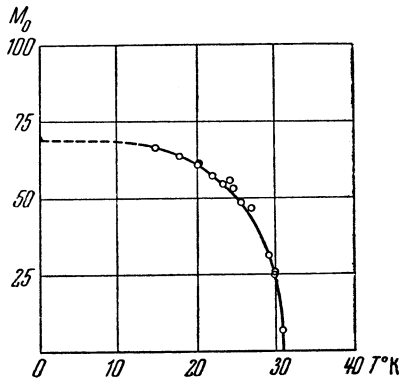


FIG. 4. Temperature dependence of  $M_0$  for  $\text{MnCO}_3$ .

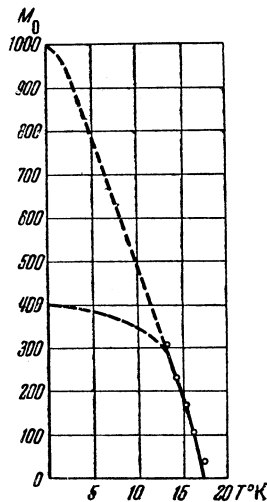


FIG. 5. Temperature dependence of  $M_0$  for  $\text{CoCO}_3$ .

We do not think that it is possible to explain the observed constant moment  $M_0$  by the presence of ferromagnetic impurities. The agreement of the results obtained on different specimens is evidence against such an explanation.

Also plotted in Fig. 6 are the values of  $1/\chi'$  calculated from our experimental data. We see that, in contrast to the usual antiferromagnetics, the susceptibility does not decrease below  $T_c$ .

It is possible to explain the results qualitatively by assuming that below  $T_c$ , in manganese and cobalt carbonates, an antiferromagnetic ordering develops. In contrast to the usual antiferromagnetics, however, the magnetization vectors of the sublattices in the present case are not exactly antiparallel to each other, but are inclined at a small angle. A similar picture of nonparallel directions

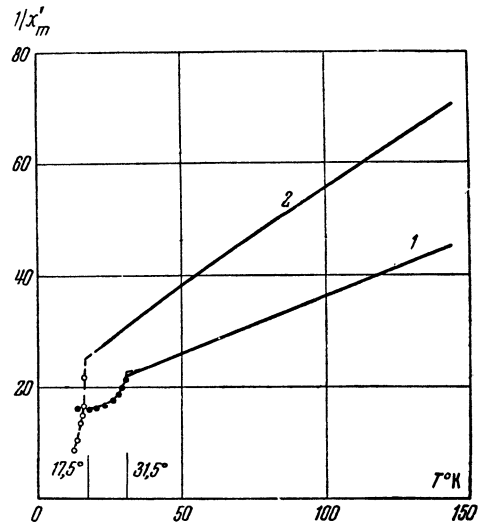


FIG. 6. Temperature dependence of the paramagnetic part of the susceptibility,  $\chi'$ : 1— $\text{MnCO}_3$ ; 2— $\text{CoCO}_3$ .

of spontaneous magnetization of the sublattices has been established by neutron diffraction for  $\text{NiFe}_2$ .<sup>7</sup> In the body-centered rhombohedral lattice of the carbonates, antiferromagnetic superexchange interaction must occur along the trigonal axis. On this axis the  $\text{CO}_3^{2-}$  groups are distributed between the metallic ions.<sup>8</sup> A small inclination (of the order of a few tens of minutes) of the direction of spontaneous magnetization with respect to the trigonal axis can be explained by the fact that the triangles of the  $\text{CO}_3^{2-}$  groups are turned through  $180^\circ$  in each successive layer. This must lead to the appearance of an uncompensated moment  $M_0$ , directed perpendicular to the trigonal axis. The magnitude of this moment will decrease with temperature along with the magnetization of the sublattices. An alternative basis of explanation of uncompensated moments in antiferromagnetic carbonates might be a difference between the effective magnetic moments of the metallic ions located at the corners and at the center of rhombohedral cell.

Which of these proposals is right might be determined by investigating the magnetic properties of monocrystals. Regrettably, an investigation that we made with a monocrystal of natural  $\text{MnCO}_3$  (rhodochrosite) showed a quite different behavior of the susceptibility, without noticeable anomalies. Evidently the isomorphic impurities unavoidably present in minerals produce changes of kind in their magnetic properties. In work of Bizette and Tsai,<sup>9</sup> the results of which came to our notice after we had finished our work, a purer mineral—dialogite ( $\text{MnCO}_3$ )—was investigated. Our results

agree qualitatively with the data for dialogite. It follows from the data of Bizette and Tsai that an uncompensated moment is directed perpendicular to the trigonal axis; this supports our first proposal.

In closing, the authors convey their profound thanks to Prof. P. G. Strelkov for his constant interest in the work.

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<sup>7</sup> R.A. Erickson, *Phys. Rev.* **90**, 779 (1953).

<sup>8</sup> B. F. Ormont, *Structure of Inorganic Substances*, Moscow-Leningrad, 1950, p. 757.

<sup>9</sup> H. Bizette and B. Tsai, *Compt. rend.* **241**, 369 (1955).

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## Dispersion Relations for Scattering and Photoproduction

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A derivation is given of the dispersion relations for the following problems: scattering of pions by nucleons (excluding the case of scattering at small but nonzero angles), photoproduction of pions on nucleons, scattering of nucleons and antinucleons by nucleons. The method of consideration is based on the general requirement of the impossibility of the propagation of signals with velocities exceeding that of light, and does not make use of the concept of the *S* matrix for demonstration of the analytical properties of the scattering amplitude. The issue is decided as to whether requirement of microcausality is a necessary condition for the validity of the dispersion relations and it is pointed out that for certain types of violation of causality, the dispersion relations are preserved.

**R**ECENTLY, Goldberger and others<sup>1-4</sup> obtained dispersion relations for the problem of the scattering of mesons from nucleons. In their derivation of the dispersion relations, these authors relied on the concept of microcausality; they made use of a series of general situations of quantum field theory in its present-day formulation. In view of the great generality of the dispersion relations, there is interest in giving another (and, as it appears to us, simpler) derivation of these relations, relying essentially only on the requirement of the impossibility of the propagation of signals with velocities greater than the velocity of light. The method set forth allows us to draw several conclusions on the problem of whether it is necessary, for the existence of dispersion relations, that the propagation velocity of the interaction be smaller than the velocity of light everywhere, even at microscopic distances (of the order of a nuclear distance), or whether it suffices to fulfill this condition only for macroscopic distances. In this case

it appears that the dispersion relations are preserved if we assume that the interaction can propagate, not inside the light cone  $t^2 - r^2 > 0$ , but inside the hyperboloid  $t^2 - r^2 > -l_0^2$  ( $l_0$  is a distance of the order of a nuclear distance), i.e., when a condition which violates causality is imposed in the interval.

In the present paper, the dispersion relations are considered for the scattering and photoproduction of pions on nucleons, and for the problem of scattering of nucleons and antinucleons by nucleons.

### 1. SCATTERING OF PIONS BY NUCLEONS

Let us consider the scattering amplitude (without charge exchange) of  $\pi^\pm$ -mesons by protons,  $f_\pm(\omega, \theta)$ , in which we first limit ourselves to the case of forward scattering\*.

\* We shall neglect Coulomb scattering.