PRNC -- 146 PUERTO RICO NUCLEAR CENTER CRYSTAL STRUCTURE OF CoBr2·6H2O AT ROOM TEMPERATURE BY NEUTRON DIFFRACTION OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT NO. AT 40-11-1833 FOR U.S. ATOMIC ENERGY COMMISSION ---Page Break--- PRNC ~ 146 PUERTO RICO NUCLEAR CENTER CRYSTAL STRUCTURE OF CoBr2·6H2O AT ROOM TEMPERATURE BY NEUTRON DIFFRACTION By Robert Kleinberg OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT NO. AT 40-11-1833 FOR U.S. ATOMIC ENERGY COMMISSION ---Page Break--- Crystal Structure of CoBr2·6H2O at Room Temperature by Neutron Diffraction * ROBERT KLEINBERG Puerto Rico Nuclear Center, and Physics Department, University of Puerto Rico at Mayaguez, Mayaguez, Puerto Rico 00708 Atomic parameters in ferromagnetic CoBr2·6H2O have been determined at room temperature from a single-crystal neutron diffraction study in which the intensities of 67 independent reflections of the h0l zone were measured. Isotropic least-squares refinement of the structure gave a final value of 0.051 for the reliability factor R. A study of the atomic parameters shows that this salt is isomorphous to cobalt and nickel chloride hexahydrate. The Co-Br and H+-Br bond lengths were found to be 2.58 Å and 2.362 Å, respectively. Unit cell parameters were found to be a = 10.93 Å, b = 6.86 Å, and γ = 124°50". Work performed under the auspices of the U.S. Atomic Energy Commission ---Page Break--- INTRODUCTION The magnetic structure and spin direction in antiferromagnetic CoCl2·6H2O has been discussed in a previous report. In the present paper, the same properties are discussed for CoBr2·6H2O. In a preliminary experiment on the latter salt, the magnetic structure was confirmed to be the same as in the chloride. An attempt to accurately determine the spin direction was not successful, since the crystal used in the experiment was not a single crystal, and neither of the individual crystallites could be aligned to give reflections exclusive of the other crystallite. It was decided, therefore, to repeat this experiment as low-temperature facilities became available.

available at the Puerto Rico Nuclear Center. Unfortunately, the crystal to be used was again composed of two crystallites, but in this case it was noted that the intensities of the reflections were quite small and were constant. It was decided to make a room-temperature study on the nOL zone, to determine just how good an R factor could be obtained with this crystal before proceeding with the low-temperature work. Further, it would be possible to confirm that the crystal structure of this salt is indeed isomorphic to that of the cobalt and nickel chlorides, and also to make a direct measurement of the Co-Br bond length. ---Page Break--- EXPERIMENTAL ‘A large crystal of CoBr2 was grown from aqueous solution at about 27°C, and had a habit similar to that of the corresponding cobalt and nickel chlorides.” The crystal was ground into a cylinder with b. Grinding was accomplished by slowly rubbing the crystal over a cloth. The cylinder obtained by this process had the dimensions: diameter = 4.2 mm; length = 7 mm. The crystal was glued to an aluminum mount and protected from the atmosphere by means of a thin-walled titanium-zirconium cap, sealed with silicone grease. Under this condition, it remained stable during the course of the experiment. Unit cell parameters were determined by measuring the coordinates of all reciprocal lattice points, ten of which were below 36° in two-theta, and then finding the parameters which gave the best least-squares fit between the measured and calculated coordinates. The quantities obtained were [Leegew7yy] of, and [Zee-497]2, parameters determined by this procedure are as follows: a = 10.93, b = 6.86, and γ = 124.50°. The wavelength used was 1.066 Å. Intensity measurements yielded 67 observed independent nOL reflections. A reflection was defined to be unobserved when from counting statistics intensity was less than three times the standard deviation. Measurements were made for theta less than 45.5°. Since the incoherent scattering from hydrogen is large, cylindrical absorption corrections were applied to each.

tn naity measurement (IR = 0.956). Absorption-correction factors were determined from Table 5.358 in the International Tables for X-Ray Crystallography.? ---Page Break--- REFINEMENT OF THE STRUCTURE by full-matrix least squares based on F, using the Los Alamos Crystal Structure Least Squares Program, cEwuzs.* twenty-five including 2 scale factors, 14 atomic parameters, 8 isotropic thermal parameters, and 1 extinction parameter, were determined from the 67 reflections. Scattering lengths for Co, Br, O, and H were assumed to be 0.250, 0.670, 0.577, and -0.376 x10"? em, respectively, and were held constant during the refinement calculation. The quantity minimized was y“ im which g {8 proportional to the secondary extinction parameter.> The $\Delta = |F|^2$, where the standard deviation of the structure factor as determined from counting statistics for observed reflections was given zero weight, and were not included in the reliability factor calculations. Refinement was continued until R < 7.6 x 10" for all least-squares parameters. At the termination of the computation, the reliability factor $R= \Sigma|Fo - Fc| / \Sigma|Fo|$ was 0.051. The root-mean-square reliability factor [Evariance/De,7] was 0.086, refined position and isotropic temperature parameters with their calculated standard deviations are given in Table 1, while the observed and calculated structure factors are listed in Table II. Structure factors calculated from unobserved intensities are enclosed in parentheses. ---Page Break--- Discussion As expected, the bromine atomic parameters are different from the chlorine parameters in cobalt chloride hexahydrate, giving a longer metal-halogen bond of 2.58 as compared to 2.43 Å for Co-Cl. The remaining parameters agree reasonably well with the corresponding parameters in the cobalt and nickel chlorides. Bond lengths and angles calculated from the parameters of Table I are listed in Table III. On comparing these results with the corresponding bond lengths in cobalt and nickel chloride hexahydrate, it is observed that.

Bond lengths involving bromine are longer than the equivalent lengths in the chlorides and fall within the expected range of values; bond lengths involving hydrogen and no bromine atoms agree within experimental error with the corresponding lengths in the nickel chloride; and bond lengths and angles within experimental error for those not involving hydrogen or bromine correspond with the lengths and angles in $CoCl_2•6H_2O$. The object of the experiment reported here was to determine the hydrogen-atom positions and to determine the feasibility of using the crystal for precise low-temperature work. An R factor indicates that the crystal should give accurate values for the magnetic properties at low temperatures, given the atom positions, as well as the Co-Br bond distance.

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TABLE I. Positional and thermal parameters in CoBr2•6H2O determined from isotropic least squares refinement of room-temperature neutron interaction data, atom x y z thermal
0.281 (4) 0.179 (2) 9.0370(7) 0.2454(9)
0.285 (1) 0.696 (2)
0.106 (1) 0.276 (2)
0.452 (1) 0.226 (3)
0.196 (2) 0.558 (3)
0.265 (3) 0.821 (3) 43

eee eee “ Throughout this paper the standard deviation of a function is given in the parenthesis following the function, and its value corresponds to least significant digits in the function value. ---Page Break--- TABLE II. Observed and calculated structure factors for CoBr■ at room-temperature neutron-diffraction data. 2 a 6 5 4 23 +2 a 1601s 453-450 188 168 ae 7456 260-195 S65 589, ee 32 ss1 550 87 18682 (19 373-370 777 356-370, (2) 26 nn? 1s qo ait 343,305, 2-99 Gp -s0 128-178 1B? 285 243 Cod i 37 “Be 1er = 174, 92 =72 229216 1st 162 36739 fo 31 336 -323 $553 see i665, 122-123 “3780 ns 123 S15 465, 238 237 a “33 52 “55 395-358 182176 (Qe) =76 Ga 269 ies an 179-175 tes 16 (35) 47 18s -196 to “a2 252-277 are 287 153 "175 (50) 3 356 04, too -91 qe 180 223-235 23-205 (s0 2 126-131 37838) 150143 375361 es) e See 450 (en) 35 439459 (28 31e -336 (ey 53 316 “336 30118 Ber -552 £0 -29 330 350 261-275 374360 103 “99 77 = 82 306 321 108 130 i32) “33 (Se 30 146-150 270-264 (ss) 67 245-238, 130159 520 S42 (4) 223 41s 62) ($3) 4) she 858, «ao ---Page Break--- TABLE III. Interatomic distances and bond angles in CoBr■ at room temperature. SS OOO co-nr co-0y, 2.58 ay) 3.94 (2) 2.98 (1) 0.89 (3) 0.99 (2) 151 (3) 3.33 @) 2.36 (2) 107 (2)? tes (1) ---Page Break---