Crystallographic symmetry and magnetic structure of CoO

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The crystallographic symmetry of antiferromagnetic CoO was studied using high-resolution synchrotron powder diffraction in the temperature range 10–300 K. The high-quality powder patterns unambiguously revealed a monoclinic symmetry (space group $C2/m$) and allowed the extraction of accurate values for the lattice constants. The temperature dependence of the monoclinic deformation scales with the much stronger tetragonal distortion as determined from laboratory x-ray diffraction. Magnetic ordering is associated with a cubic-to-monoclinic transition that is, thus, of first order. Neutron powder-diffraction data are compatible with a collinear magnetic structure with the moments ordered in the monoclinic ac plane.

Paramagnetic CoO has the NaCl-type crystal structure (space group $Fm3m$). In the antiferromagnetic state ($T_N \simeq 290$ K) it shows a large tetragonal distortion along cube edges with $c/a < 1$.[1,2] An additional deformation along the $\langle 111 \rangle$ direction has been inferred from a faint splitting of a Bragg reflection observed in a single-crystal x-ray oscillation photograph.[3] The combined effect of the two distortions is to reduce the symmetry to monoclinic. The splitting, however, was not confirmed by other investigators. Birefringence has been observed with the direction of light parallel to the c axis,[4] which can be ascribed to monoclinic symmetry but equally well to internal strain. Despite the long tradition of attention to CoO, which is frequently cited as an archetypal antiferromagnetic Mott-type insulator, its real structure has not been determined unambiguously up to now.

Compatibility between crystallographic symmetry and the possible magnetic structures of CoO has been the subject of continuous debate over the last 40 years. All studies agree on a magnetic configuration of propagation vector $\mathbf{k} = [1/2, 1/2, 1/2]$, referred to the cubic unit cell, as first described by Shull, Strauser, and Wollan.[5] Three different moment directions were reported for a collinear arrangement of ferromagnetic sheets on (111) planes: along the tetragonal axis,[5] along a direction that makes an angle of 11.5° with respect to the c axis,[6] and eventually a direction with a tilt angle of 27.4°.[7] A collinear structure with a finite tilt angle is not compatible with the retention of tetragonal symmetry, and a multi-spin-axis structure that preserves tetragonality and gives equivalent magnetic moments was suggested by Van Laar.[7] From single-crystal neutron diffraction under various uniaxial stress directions, Herrmann-Ronzaud, Barlet, and Rossat-Mignod[8] concluded that the magnetic structure must be collinear with the moments making an angle of about 25° with the c axis.

In order to come to a conclusive answer about the crystal symmetry and magnetic structure of CoO we have performed powder-diffraction studies using synchrotron radiation at European Synchrotron Radiation Facility (ESRF), neutrons and laboratory x rays at the Hahn-Meitner-Institut (HMI). This work is part of a broader study devoted to the electron-density distribution in CoO.

The measurements were performed on a polycrystalline specimen from Alfa Chemical Company. Besides the expected lines for CoO, the neutron-diffraction pattern revealed the presence of the impurity Co_3O_4 at a concentration of 13%. In order to relieve internal strains that could compromise the resolution of the synchrotron experiment, the higher oxide was reduced by annealing a sample at 1000 °C and cooling slowly to room temperature in a stream of argon.

A Guinier focusing monochromator diffractometer with a Cu anode ($\lambda = 1.540598$ Å), equipped with a closed cycle helium refrigerator, was employed first. The range of 2θ was restricted to a maximum value of 100°. No deviation from tetragonal symmetry could be evidenced. Figure 1 (top) shows the temperature dependence of the tetragonal contraction of the pseudocubic cell, $1 - c/a$, as derived from Gaussian fits to the 200/002 reflections. Above 265 K the lines are no longer resolved but the full width at half maximum $\Delta\theta$ increases linearly with decreasing temperature from 0.064° at 290 K to 0.095° at 270 K. The lattice constant at 305 K was determined to be $a = 4.2614(3)$ Å, which is in good agreement with previously published values. Angular calibration of the observed 2θ's was performed by means of a least-squares refinement of several silicon powder peaks. At 10 K, the cell parameters of the deformed face-centered lattice are $a = 4.2666(3), c = 4.2151(4)$ Å.

The high-resolution powder diffractometer on the BM1B (Swiss-Norwegian beam line) at ESRF was used with $\lambda = 0.50084$ Å in a further effort to clarify the true symmetry of CoO. The sample was filled in a 0.5 mm diameter capillary. Complete powder patterns with a 2θ range between 1° and 62° were collected at 10 and 293 K. The sample was cooled by means of a liquid-helium cryostat with a temperature stability of ±0.1 K. At the temperatures between 30 and 200 K only partial patterns were recorded. Further data between 150 and 300 K were collected on BM16 with $\lambda = 0.40578$ Å using a cryostream nitrogen cooling system with a poorer stability of ±5 K. As can be seen in Fig. 2, the presence of a monoclinic lattice is clearly manifested by a splitting of the reflections. Rietveld refinements on each powder pattern were performed making use of FULLPROF.[9]
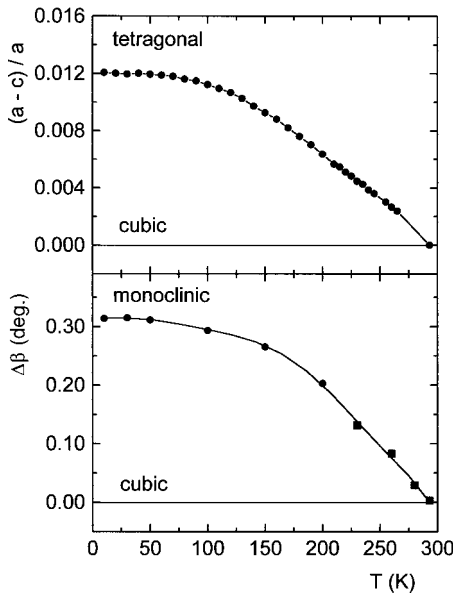
FIG. 1. Top: The tetragonal distortion of the pseudocubic cell (four CoO units per cell) versus temperature as obtained from laboratory x rays. Bottom: The monoclinic deformation angle $\Delta\beta$ (space group $C2/m$ with two CoO units per cell) versus temperature as obtained from synchrotron x rays. Circles refer to BM1B data, squares to BM16 data with a poorer temperature stability. The standard deviations are all smaller than the size of the symbols.

All peaks were indexed in the space group $C2/m$ with Co at position $2a(0,0,0)$ and O at $2d(0,1/2,1/2)$. Additional peaks revealed that the impurity Co_3O_4 was still present at a concentration of 5%, and it was included in joint refinements. The monoclinic angle may be written as $125.2644° + \Delta\beta$, with $\Delta\beta$ referring to the deviation from orthogonality of the conventional face-centered cell. The relationship between the monoclinic unit cell and the original cubic cell is illustrated in Fig. 3. Experimental results for $\Delta\beta$ as a function of temperature are shown in Fig. 1 (bottom). It is apparent that the temperature dependence of the monoclinic deformation scales with the much stronger tetragonal distortion. The an-
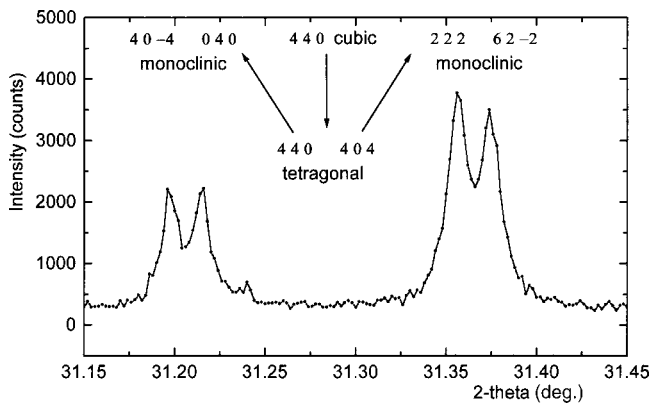

FIG. 2. Section of the synchrotron diffraction pattern at 150 K, showing the emergence of monoclinic splitting. The cubic 440 reflection (space group $Fm3m$) splits into the tetragonal reflections 440/404, which further split into the monoclinic reflections 40-4/040 and 222/62-2 (space group $C2/m$).
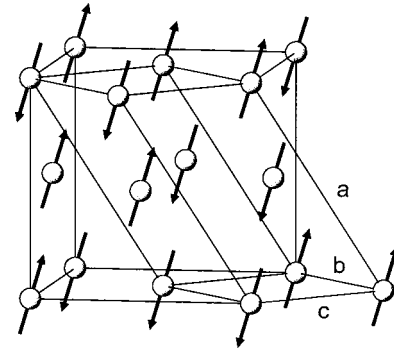

FIG. 3. The monoclinic unit cell of antiferromagnetic CoO related to its paramagnetic structure. The magnetic structure of monoclinic symmetry is shown with the moments ordered in the ac plane.

tiferromagnetic transition is thus accompanied by a cubic-to-monoclinic crystallographic distortion. At 293 K, the lattice constant of the cubic phase is $a = 4.260\,77(2)$ Å. At 10 K, the monoclinic lattice constants are $a = 5.181\,90(6)$, $b = 3.017\,61(3)$, $c = 3.018\,60(3)$ Å, $\beta = 125.5792(9)°$. In the face-centered setting, this corresponds to an angle of 89.962° between the two edges of different length. It is important to note that the result reported in Ref. 3, $\Delta\beta(125\text{ K}) = 0.303°$, has been confirmed at a quantitative level.

Neutron powder diffraction ($\lambda = 2.43$ Å) was performed on the instrument E6 at the BERII reactor. The scattering angle range covered 15°–105°. Data were recorded at $T = 60$ K well above $T_N(Co_3O_4) = 40$ K. Again, both phases of cobalt oxide were included in the Rietveld refinement (monoclinic CoO: five nuclear and eight magnetic reflections). The propagation vector $\mathbf{k} = [1/2, 1/2, 1/2]$, referred to the cubic cell, splits into two vectors $\mathbf{k}_1 = [0, 1, 1/2]$ and $\mathbf{k}_2 = [1/2, \pm 1/2, 0]$, referred to $C2/m$. The vector $\mathbf{k}_1$ has a single-arm star and the magnetic moments are either along the twofold axis or in the mirror plane, i.e., monoclinic symmetry is preserved. The second vector has a double star and the moments are out of any symmetry element. The orientation of the moments is defined by the angle θ (between moment direction and the twofold axis b) and the angle φ (between moment direction and the a axis within the ac plane). In the magnetic structure refinements the lattice parameters were fixed to the values obtained from the synchrotron experiment. The $\mathbf{k}_1$ structure with $\theta = 0°$ gives $R_M = 0.20$ (magnetic R factor $R_M = \Sigma|I_{obs} - I_{cal}|/\Sigma I_{obs}$). In view of the large value of R_M, this model is clearly discarded by our data. The $\mathbf{k}_1$ structure with $\theta = 90°$ gives $R_M = 0.046$ and fixes the moment direction to $\varphi = 55(2)°$. A magnetic moment of $3.98(6)\mu_B$ per cobalt ion is found, which is close to the previously reported value of $3.8\mu_B$.[6,8] It is considerably larger than the pure spin moment of $3\mu_B$. The Co orbital magnetic moment is calculated in recent theoretical studies[10,11] to be about $1\mu_B$. Refinement of a collinear $\mathbf{k}_2$ structure (single-channel transition) yields $\theta = 71(2)°$ and $\varphi = 28(5)°$ with the same amplitude of the magnetic moment and $R_M = 0.045$. A collinear structure of triclinic symmetry is therefore also compatible with the observed diffraction pattern. A noncollinear $\mathbf{k}_2$ structure requires perpendicular directions for the two Fourier components in order to obtain

constant moments. Refinements resulted in large R factors so the noncollinear model can be excluded, a result that had already been arrived at by Herrmann-Ronzaud, Barlet, and Rossat-Mignod.[8] The magnetic structure of monoclinic symmetry is shown in Fig. 3.

Cobalt with the $3d^7$ configuration in the high-spin arrangement, when embedded in a cubic crystal electric field, has a single hole in the triplet t_{2g} shell and according to the Jahn-Teller effect, the hole should be stabilized by a lifting of the perfect octahedral symmetry. For the t_{2g} levels, there are two Jahn-Teller active vibrational modes, E_g and T_{2g}, with the first one leading to tetragonal and the latter one to trigonal symmetry. The seemingly exclusive existence of a tetragonal distortion in CoO has indeed been cited as a case of Jahn-Teller distortion with compression of the octahedron.[12] In this case, however, the transition would be a purely structural one. Since the symmetry reduction is to monoclinic and occurs simultaneously with magnetic ordering, magnetostriction is the more plausible cause for the crystallographic distortion. This is substantiated by the ex-ample of MnO, which is not a Jahn-Teller case but neverthe-less exhibits a pronounced rhombohedral distortion below T_N.

Finally, our results throw light on the nature of the phase transition in CoO. The theory of the phase transitions in the transition-metal monoxides has been discussed by Mukamel and Krinsky.[13] This theory predicts that these systems should show first-order transitions. The prediction is supported by the present study since a cubic-to-monoclinic symmetry breaking is incompatible with a continuous second-order transition. The first-order jump and the temperature hysteresis must be very small in CoO. No first-order discontinuity (and no second phase transition close to T_N) was observed with highly sensitive birefringence measurements.[4] In general, it is often difficult to establish experimentally whether or not there is a discontinuity in a particular quantity at the transition temperature and a decision based on symmetry is by far the more direct one.

[1] N. C. Tombs and H. P. Rooksby, Nature (London) **165**, 442 (1950).

[2] S. Greenwald, Acta Crystallogr. **6**, 396 (1953).

[3] S. Saito, K. Nakahigashi, and Y. Shimomura, J. Phys. Soc. Jpn. **21**, 850 (1966).

[4] K. H. Germann, K. Maier, and E. Strauss, Phys. Status Solidi B **61**, 449 (1974).

[5] C. G. Shull, W. A. Strauser, and E. O. Wollan, Phys. Rev. **83**, 333 (1951).

[6] W. L. Roth, Phys. Rev. **110**, 1333 (1958).

[7] B. Van Laar, Phys. Rev. **138**, A584 (1965).

[8] D. Herrmann-Ronzaud, P. Barlet, and J. Rossat-Mignod, J. Phys.

C **11**, 2123 (1978).

[9] J. Rodriguez-Carvajal, FULLPROF: a Program for Rietveld Refinement and Powder Matching Analysis, Abstract of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr (IUCr, Toulouse, 1990), p. 127.

[10] T. Shishidou and T. Jo, J. Phys. Soc. Jpn. **67**, 2637 (1998).

[11] I. V. Solovyev, A. I. Liechtenstein, and T. Terakura, Phys. Rev. Lett. **80**, 5758 (1998).

[12] K. I. Kugel and D. I. Khomskii, Usp. Fiz. Nauk. **136**, 621 (1982) [Sov. Phys. Usp. **25**, 231 (1982)].

[13] D. Mukamel and S. Krinsky, Phys. Rev. B **13**, 5078 (1976).