Neutron-Diffraction Investigation of CoO Single Crystals

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Neutron-diffraction data have been obtained from CoO single crystals, cooled down through the Néel point, while applying a small pressure. Thus, crystallographically almost untwinned, tetragonal crystals were obtained. The observed intensities can be explained either by the collinear-spin model given by Roth, with the assumption that any of the four possible antiferromagnetic domains occurs with exactly the same volume, or by the multi-spin-axis model proposed by van Laar. The results are compared with magnetic-torque measurements.

INTRODUCTION

A TETRAGONAL deformation is shown by CoO (which has cubic symmetry in the paramagnetic state) when it is cooled down through the Néel point (291°K). Its magnetic structure has been studied by Shull, Strauser, and Wollan,[1] Roth,[2] and recently van Laar.[3] Both Shull *et al.* and Roth proposed a collinear model, based on ferromagnetic sheets of moments, parallel to (111) planes.

Roth derived that the antiferromagnetic spin axis is in the $(1\bar{1}0)$ plane with an angle of 11.5° between this axis and the tetragonal c axis. van Laar, whose data were taken with a diffractometer with a much higher resolution than Roth's, was able to show that the angle between the spin axis and the c axis is 27.4° instead of 11.5°, assuming the collinear-spin model to be correct. He also proposed a multi-spin-axis model which is strictly tetragonal, in conformity with the crystallographic deformation. The collinear model, which has rhombohedral symmetry, fails to explain this deformation.

As the collinear and the multi-spin-axis model give exactly the same powder neutron-diffraction intensities, it was impossible to distinguish between these models and powder data. With a single-crystal sample the multi-spin model leads to the same intensities for the four magnetic reflections (hkl), $(\bar{h}\bar{k}l)$, $(\bar{h}kl)$, and $(h\bar{k}l)$, while in the collinear model only one of these intensities is nonzero and accounts for the full powder intensity. Thus it should be possible to distinguish between these two models with single-crystal data. For this reason the present work has been undertaken.

EXPERIMENTAL

The crystals that were used were kindly furnished by J. Mareschal of the Centre d'Etudes Nucléaires de Grenoble (CENG). After cutting from an ingot, grown by the Verneuil-method, they were annealed for 48 h at 1000°C and cooled down slowly in a stream of argon.

Measurements were carried out on two different crystals, which we shall designate as A and B. Crystal A had been ground to 5.25×2.50×2.50 mm, thus having a perfectly square prismatic shape; crystal B was untouched after the cleavage and measures 4.52×3.40×3.56 mm.

As there are three possible directions for the tetragonal axis when the crystal becomes antiferromagnetic, in general CoO shows crystallographic twinning below the Néel point. Uchida *et al.*[4] indicate a method to obtain an almost untwinned antiferromagnetic single crystal. Following this method, we mounted the crystal in a liquid-nitrogen cryostat, so that it was cooled down in a temperature gradient while a small pressure in the vertical direction was applied (Fig. 1). The whole cryostat was mounted on a goniometer head. The monochromator used was a Ge crystal [(113) plane]. The neutron wavelength was 1.127 Å.

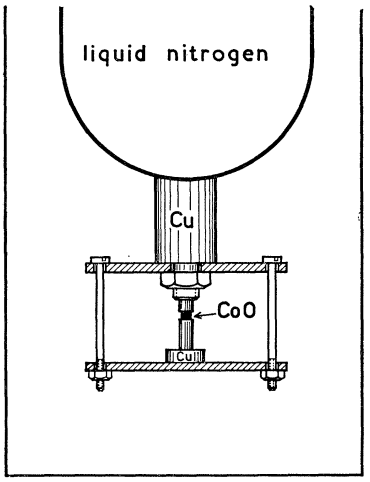

FIG. 1. Mounting of the crystal in the cryostat thus permitting it to cool down in a temperature gradient and a small vertical pressure.

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[3] B. van Laar, Phys. Rev. **138**, A584 (1965).
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TABLE I. Observed intensities from CoO single crystals in the antiferromagnetic state. The intensities are given as fractions of the sum of the intensities of the reflections (hkl), $(\bar{h}\bar{k}l)$, $(\bar{h}kl)$, and $(h\bar{k}l)$. The stated uncertainties are calculated from statistical counting errors. For crystal B, data are given for successive cooling and rewarming cycles.

		Crystal B		
(hkl)	Crystal A	1st cycle	2nd cycle	3rd cycle
040	0.256±0.004	0.253±0.002		
400	0.245	0.245		
0$\bar{4}$0	0.253	0.257		
$\bar{4}$00	0.246	0.245		
440	0.254±0.005	0.252±0.002		
$\bar{4}\bar{4}$0	0.249	0.255		
$\bar{4}$40	0.249	0.247		
4$\bar{4}$0	0.248	0.246		
222	0.260±0.006	0.252±0.004		
$\bar{2}\bar{2}$2	0.260	0.254		
$\bar{2}$22	0.235	0.246		
2$\bar{2}$2	0.245	0.248		
622		0.248±0.005		
$\bar{6}\bar{2}$2		0.253		
$\bar{6}$22		0.251		
6$\bar{2}$2		0.248		
262		0.252+0.005		
$\bar{2}\bar{6}$2		0.252		
$\bar{2}$62		0.250		
2$\bar{6}$2		0.246		
111	0.251±0.002	0.260±0.002	0.262±0.004	0.255±0.004
$\bar{1}\bar{1}$1	0.251	0.248	0.244	0.251
$\bar{1}$11	0.248	0.250	0.250	0.251
1$\bar{1}$1	0.251	0.242	0.244	0.244
311	0.253±0.004	0.267±0.003	0.268±0.005	0.263±0.006
$\bar{3}\bar{1}$1	0.252	0.250	0.248	0.257
$\bar{3}$11	0.248	0.251	0.255	0.246
3$\bar{1}$1	0.247	0.232	0.229	0.235
131	0.246±0.004	0.233±0.003		0.234±0.005
$\bar{1}\bar{3}$1	0.250	0.252		0.251
$\bar{1}$31	0.248	0.254		0.247
1$\bar{3}$1	0.256	0.262		0.269
331	0.250±0.010	0.247±0.005		0.243±0.007
$\bar{3}\bar{3}$1	0.253	0.252		0.260
$\bar{3}$31	0.245	0.241		0.244
3$\bar{3}$1	0.252	0.261		0.253
511	0.254±0.010	0.264±0.005		0.266±0.009
$\bar{5}\bar{1}$1	0.255	0.254		0.250
$\bar{5}$11	0.238	0.248		0.243
5$\bar{1}$1	0.254	0.235		0.240
151	0.249±0.010	0.256±0.005		0.262±0.009
$\bar{1}\bar{5}$1	0.248	0.247		0.242
$\bar{1}$51	0.258	0.252		0.258
1$\bar{5}$1	0.245	0.244		0.239
313	0.237±0.010	0.239±0.005		
$\bar{3}\bar{1}$3	0.264	0.239		
$\bar{3}$13	0.233	0.249		
3$\bar{1}$3	0.260	0.272		
133	0.235±0.010	0.261±0.005		
$\bar{1}\bar{3}$3	0.254	0.246		
$\bar{1}$33	0.235	0.248		
1$\bar{3}$3	0.277	0.245		
333	0.245±0.010	0.271±0.005		
$\bar{3}\bar{3}$3	0.254	0.241		
$\bar{3}$33	0.232	0.248		
3$\bar{3}$3	0.269	0.240		

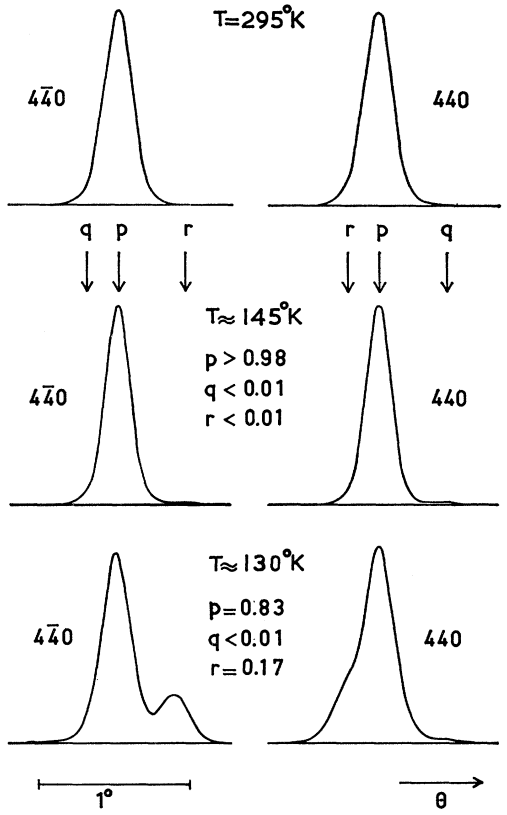

FIG. 2. Peak shapes of the (440) and the (4$\bar{4}$0) reflections from a crystal at room temperature, crystal B ($T\approx145$°K, practically untwinned), and crystal A ($T\approx130$°K, partially twinned), respectively. The arrows, marked p, q, and r indicate the calculated positions of the peak, due to the different crystallographic twins.

Since it was impossible to rotate the sample around any other axis than the vertical one, the only possibility to collect the intensity data was by using a rotating crystal method with the counter arm tilted to the desired angle. This facility is available at the DN2 diffractometer, located at the Melusine reactor of the CENG.

It should be noted that it was only the intention to compare intensities in a group (hkl), $(\bar{h}\bar{k}l)$, $(h\bar{k}l)$, and $(\bar{h}kl)$. The sum of these intensities is known from the powder work.[3]

Intensities from crystal A have been taken once, those of crystal B three times with intermediate heating to above the Néel point and recooling.

RESULTS AND INTERPRETATION

The observed intensities in each group of four reflections are practically equal (Table I). We designate as p, q, and r the volume fractions of the crystal, tetragonalized along the three possible directions. The values of p, q, and r can be measured at the (440) and (4$\bar{4}$0)

reflections. In these reflections the angular separation of the intensities due to the different twins is large enough to separate the intensities quite accurately (Fig. 2). For crystal A this resulted in: $p=0.83$, $q=0$, $r=0.17$, for crystal B in each of the three series of measurements p was greater than 0.98 and this crystal can be considered as practically untwinned. The two spin models will be discussed separately.

Collinear Model

In this model we have to consider the possibility of the existence of four different directions of the antiferromagnetic axis in each tegragonal twin p, q, and r. The fractions of these domains in part p are denoted by α_p, β_p, γ_p, and δ_p, etc. When the magnetic domain α_p is in reflection position for its reflection (hkl), the intensity is given by

$$I(hkl) \propto p[\alpha_p F(hkl)^2+\beta_p F(\bar{k}hl)^2+\gamma_p F(\bar{h}\bar{k}l)^2+\delta_p F(k\bar{h}l)^2] +q[\alpha_q F(klh)^2+\beta_q F(l\bar{k}h)^2+\gamma_q F(kl\bar{h})^2+\delta_q F(l\bar{k}h)^2] +r[\alpha_r F(lhk)^2+\beta_r F(\bar{h}lk)^2+\gamma_r F(lh\bar{k})^2+\delta_r F(\bar{h}l\bar{k})^2]\cdots. \quad (1)$$

In this expression $F(hkl)$ denotes the structure factor, calculated for domain α_p.

From the results on crystal A the magnetic domain distribution in each twin is calculated by means of a least-squares method. This resulted in

$$\alpha_p=0.256\pm0.006, \quad \alpha_r=0.22\pm0.03,$$
$$\beta_p=0.246\pm0.006, \quad \beta_r=0.23\pm0.03,$$
$$\gamma_p=0.247\pm0.006, \quad \gamma_r=0.28\pm0.03,$$
$$\delta_p=0.251\pm0.006, \quad \delta_r=0.27\pm0.03.$$

For crystal B

$$\alpha_p=0.260\pm0.004,$$
$$\beta_p=0.241\pm0.004,$$
$$\gamma_p=0.246\pm0.004,$$
$$\delta_p=0.253\pm0.004.$$

These last values deviate slightly from 0.25, but the fact that the measurements, when repeated after a heating and cooling cycle, could be reproduced within statistical counting errors proves that the deviations are not due to a nonequal distribution of the domains but that absorption effects and small systematic errors only are responsible for them.

Thus the results show clearly that, if the collinear model is correct, it is necessary to assume in each crystallographic twin any of the four possible antiferromagnetic domains to occur with exactly the same volume.

Multi-Spin-Axis Model

In this model the intensity of a reflection (hkl) is given by

$$I(hkl) \propto pF(hkl)^2+qF(klh)^2+rF(lhk)^2\cdots. \quad (2)$$

From this expression it is seen that for the multi-spin model the intensity is always equally distributed among the four reflections (hkl), $(\bar{h}\bar{k}l)$, $(\bar{h}kl)$, and $(h\bar{k}l)$ This is true even when the crystal is crystallographically twinned. Thus it is not necessary to assume a completely homogeneous distribution of the antiferromagnetic domains in order to obtain a good fit with the experimental data.

COMPARISON WITH MAGNETIC MEASUREMENTS

Magnetic-torque measurements have been carried out by Uchida *et al.*[4] on axially cooled single crystals. They found that the torque curves for rotation around [100] and [010] had the same amplitude and practically the same phase angle of $\pm3°$. The torque amplitude for the [001] rotation was much smaller and varied with the sample and its thermal treatment. They explained this varying nonzero [001] amplitude on the basis of the collinear model with the assumption that the distribution for the four possible magnetic domains was not homogeneous. This domain structure was supposed to vary with the sample treatment.

Torque data for the [001] rotation are given in detail by Nagamiya *et al.*[5] Since these data indicate a phase angle of about 45° it is deduced that the crystals were practically crystallographically untwinned. Calculation shows that, if the collinear model is correct, the volume fraction of uncompensated magnetic domains should lie between 10 and 30%. This differs from our conclusions.

If the torque measurements are explained on the basis of a multi-spin-axis model[6] the amplitude of the [001] torque should be zero independent of the domain distribution. In any case the nonvanishing [001] torque is in disagreement with the results presented in this paper.

ACKNOWLEDGMENTS

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