PHYSICAL REVIEW B VOLUME 15, NUMBER 9 1 MAY 1977

Magneto-optical observations of the magnetic domains in the nearly-two-dimensional Heisenberg ferromagnet $(C_3H_7NH_3)_2CuBr_4$

H. van Kempen, F. H. Mischgofsky,* and P. Wyder
Physics Laboratory and Research Institute for Materials, University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands

(Received 20 October 1976)

We studied the magnetic behavior of $(C_3H_7NH_3)_2CuBr_4$ crystals by means of the Faraday effect. We observed that at low temperature the crystals can exist in two crystallographic modifications. One modification shows, below the magnetic transition temperature, magnetic domains in zero magnetic field. This modification can be described by the *Pb′c′a* structure, the spins being in the *bc* plane with an angle between spins and *b* axis of 24°. The other crystallographic modification shows domains in the field range between 215 and 350 Oe. This modification can be described by a *Pb′ca′* structure at fields lower than 215 Oe, a *Pb′c′a* structure at fields higher than 350 Oe while in the field range of 215–350 Oe are alternating domains of *Pb′c′a* and *Pb′ca′* structure. The coexistence of the two magnetic structures in the field range of 215–350 Oe shows that the field-induced phase transition from the *Pb′ca′* structure to be *Pb′c′a* structure is a first-order phase transition.

INTRODUCTION

The series of compounds $(C_nH_{2n+1}NH_3)_2CuX_4$, where X represents a Cl or Br atom and n varies from 1 to 10, have been studied intensively lately because these compounds are good examples of nearly perfect two-dimensional Heisenberg ferromagnets.[1-5] The orthorhombic crystals consist of nearly quadratic layers of CuX_2 (in the *ab* plane) separated by two layers of nonmagnetic $C_nH_{2n+1}NH_3X$. The detailed crystal structure of some of the Cl compounds has been determined and is found to crystallize in the *Pbca* space group.[6,7] However, for nearly all the compounds the dimensions of the unit cell have been determined by Kop.[8] Recently Daoud[8] extended the list of known structures and found also the *Pbca* structure for the Br compounds at room temperature.

The magnetic interaction within the CuX_2 layer is ferromagnetic and is very strong compared with the interaction between the layers. Although according to the theory of Mermin and Wagner[9] an ideal two-dimensional Heisenberg ferromagnet should not have long-range order above 0 K, these compounds show an anomaly in the susceptibility at a temperature (T_c) of approximately 10 K. At this temperature the magnetic system orders in a three-dimensional way as can be concluded from the occurrence of magnetic domains in some of the compounds below T_c.[10] T_c is determined mainly by the strong intralayer exchange interaction. However, which three-dimensional magnetic structure exists below T_c is determined by small deviations from the ideal such as the interlayer interactions and the anisotropy energies. Within the series one can find ferromagnetic, antiferromagnetic, and canted antiferromagnetic stacking of the ferromagnetic layers.

In the present paper we describe observations, made by means of the Faraday effect, of the weak ferromagnetic domains in *bis* (propylammonium) copper(II) tetrabromide, $(C_3H_7NH_3)_2CuBr_4$. We observed that around or somewhat below liquid-nitrogen temperature often, but not always, a crystallographic phase transition takes place. Two different magnetic structures exist below T_c depending on the occurrence of this structural phase transition.

EXPERIMENT

The observations of the domains were carried out by means of the Faraday effect. At room temperature the $(C_3H_7NH_3)_2CuBr_4$ crystals are very opaque in the visible-light range up to about 0.6 μm; only in the red the crystals are somewhat transparent. During cooling the crystals become more transparent, but still very thin (less than 100 μm) crystals were needed to have enough light for our microscopic observations. The crystals were grown in the form of thin platelets, perpendicular to the *c* axis, of 20 to 100 μm in thickness and up to 5 mm in diameter. They were made by evaporation of a solution of the compound in water or in ethyl-alcohol. The samples made from the ethyl-alcohol solution shattered less frequently during cooling.

The apparatus is fully described elsewhere.[11] It consisted of a glass Dewar with optical windows in the bottom. Under the Dewar a polarizing microscope was placed with objective lenses with long working distance. The optical resolution was 1 μm. Light reached the sample via a rotatable light guide with a polarizer on its lower end. Both broadband and filtered light were used. The filter was transparent for wavelengths above 0.6 μm.

The samples were mounted with the *c* axis along the line of sight between two copper grids on which an Allen-Bradley carbon thermometer was glued or were placed free on the bottom glass window.

The magnetic domains could be photographed, but long time exposures were needed due to the low transparency and because the domains were only observable between almost-crossed polarizers near the extinction position of the birefractive crystals. Moreover, too much light on the sample will heat the sample relative to the carbon thermometer. There was not enough light to photograph directly the fast crystallographic phase transition, so in that case we used a video camera with image intensifier.[12] A small superconducting magnet supplied the magnetic field along the direction of the light path, that is the *c* axis direction. During the period that the liquid-helium level was between the sample and the bottom of the solenoid space the sample warmed sufficiently slowly to allow measurements up to 12 K.

OBSERVATIONS

During cooling to liquid-helium temperature we observed the birefractive crystals in the extinction position between almost-crossed polarizers. We found that large crystals showed a sudden change in brightness, caused by a rotation of the extinction axis, at some temperature below 100 K. This shows that these crystals underwent a structural phase transition. However, some minor parts of the crystals and some tiny crystallites did not show the phase transition. Because our apparatus was not adapted for temperature control in the temperature range of this phase transition we can only make a rough estimate of the transition temperature: 70 ± 20 K. In the larger crystals it was possible to observe the nucleation and growth of the low-temperature phase. The low-temperature phase nucleated somewhere in the form of a spike and expanded over the whole crystal in a few seconds with a speed of a few 100 μm/sec. During the transitions the boundaries between the phases formed almost parallel straight lines. After the transition often new twins in the *ab* plane were present. Parts of the crystals which underwent the phase transition on one cool-down could stay unchanged during a subsequent cool-down and vice versa. Very small crystallites usually did not exhibit the phase transition. Hereafter we call the crystalline parts which underwent the phase transition type *A*, the other parts, type *B*. Crystalline parts of type *A* are generally larger and optically more perfect than those of type *B*. Sometimes the crystals shattered during cooling or warming. However, when they were mounted carefully, strain free and not grown onto a substrate they generally survived unimpaired.

FIG. 1. Domains in zero applied field in type-*A* crystals at $T = 2$ K. The contrast is enhanced by photographic methods.

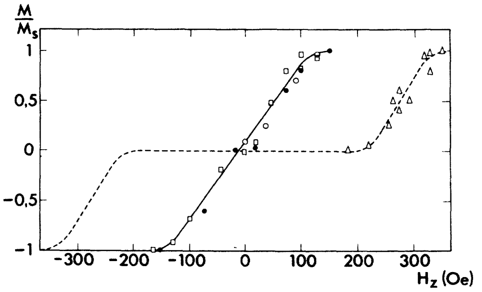

FIG. 2. Magnetization *M* versus applied field *H* for four different samples. The magnetization *M* is plotted relative to the single domain magnetization M_S. The magnetization is deduced from the dimensions of the domains by direct microscopic observation (●) or by measuring the micrographs (○,□,△). The data points in this figure were taken at 2 K, but can be considered within our accuracy to represent the situation at 0 K.

Below a transition temperature $T_c = 10.2 \pm 0.5$ K type *A* showed magnetic domains in zero applied field. The domains were straight and parallel (Fig. 1). The width depended on the sample thickness and varied from 2.5 to 4 μm for samples from 20 to 100 μm thick. When a magnetic field was applied in the *c* direction one type of domain grew at the expense of the other until at about 180 Oe the single domain state was reached (Fig. 2).

FIG. 3. Domains in a type-*B* crystal in an applied field of 280 Oe at $T = 2$ K.

After the field was removed the domains returned, however, no longer straight but quite twisted. When the temperature was raised close to T_c the domains straightened out again.

Type *B* did not show domains at zero applied field. At a field of about 215 Oe domains started to appear and grew with increasing field. (Some traces of domains were already visible at 190 Oe). At 280 Oe one type of domain covered about half the surface (Fig. 3) while at 350 Oe the single domain state was reached (Fig. 2). The observed process is typical for a field-induced first-order phase transition in which case the transition is spread out over a certain field range due to the presence of demagnetizing fields.[13] The critical temperature T_c for type *B* is 10.5 ± 1 K. The large uncertainties in the critical temperatures are mainly due to the heating effect of the polarized light beam on sample and thermometer which have only limited heat contact in the helium gas. In contrast to the straight and parallel domains of type *A*, the domains of type *B* are very twisted, branched and often of short length (Fig. 3).

DISCUSSION

Structural phase transitions have also been observed in crystal having a composition and structure related to our copper bromine compound $(CEH_7NH_3)_2CuBr_4$. For some of the $(C_nH_{2n+1}NH_3)_2MCl_4$ compounds with M = Mn, Cd, or Fe and $n = 1$, a high-temperature tetragonal phase is followed by a room-temperature orthorhombic phase and a low-temperature tetragonal phase.[14-19] For the compounds with $n = 2$, 3 and M = Mn, Cd a transition to a low-temperature *Pbca* phase has been observed.[20,21] Recently also a series of structural phase transitions has been found in copper bromine compounds with short alkylamine chains ($n < 5$), by means of differential thermal analyses, microscopic observations, transmission spectroscopy, and Guinier powder diffraction.[22] The transitions can be explained by changes in the motions of the alkylamine groups.[17-19] Far-infrared experiments at our laboratory on the copper chlorine compounds indicate a change in the vibrational modes of the metal halogen planes at the transition temperature.[23,24]

Our optical observations show that the structural phase transitions in $(C_3H_7NH_3)_2CuBr_4$ do not always take place in the same way. As a result two different crystallographic modifications exist at low temperatures which have also different magnetic properties. Susceptibility measurements of de Jongh[25] on $(C_3H_7NH_3)_2CuBr_4$ showed that a single crystal gives a susceptibility peak at $T_c = 10.3$ K while a powder sample has an additional peak at $T_c \approx 11.4$ K. On repeated heating and cooling of the single crystal, it started to shatter and the susceptibility peak at 10.3 K decreased while a peak at 11.4 K developed. This shows that also in his experiment two modifications existed; one mainly in large single crystals with $T_c = 10.3$ K, and one mainly in powderlike crystallites with $T_c = 11.4$ K. It suggests that our type *A* has the same modification as the one with $T_c = 10.3$ K and type *B* as the one with $T_c = 11.4$ K.

For $(C_3H_7NH_3)_2CuBr_4$ the lowest structural phase transition takes place between 90 and 50 K. (This result of our optical experiment is confirmed by other experiments.[22]) No structural data below this temperature are known. However, the presence of twins in the *ab* plane and the existence of a low-temperature *Pbca* structure in the Mn and Cd compounds with $n = 3$,[20,21] suggest a low-temperature orthorhombic structure also for our compound. Moreover, the low-temperature magnetic measurements of the Amsterdam group[5,26] show that both the Cl and Br compounds can very well be described by assuming the orthorhombic *Pbca* symmetry. So apparently any deviation from this symmetry is small. Therefore we will discuss our observations hereafter assuming our compound has the *Pbca* symmetry.

Bloembergen *et al.*[5] have shown with group-theoretical methods that assuming two-sublattice antiferromagnetism with the layers belonging alternately to sublattice 1 and 2, four kinds of magnetic structures are possible for the *Pbca* crystal structure. Only one of these four structures gives a weak ferromagnetic moment along the *c* axis, namely the *Pb'c'a* structure and so corresponds to type *A*. This structure has the following spin components for sublattice 1 and 2 [Fig. 4(a)]:

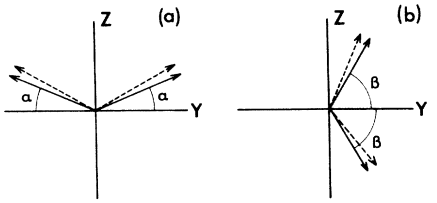

FIG. 4. Directions of the sublattice magnetization in the *Pb′c′a* structure (a) and in the *Pb′ca′* structure (b). The dashed arrows indicate the directions of the sublattice magnetization when a small magnetic field is applied in the *z* direction.

$$S_{1x}=S_{2x}=0;\quad S_{1y}=-S_{2y};\quad S_{1z}=S_{2z}$$

with the x, y, and z directions along the crystallographic a, b, and c axes, respectively. For this structure the general expression[5] for the free energy F in the molecular-field approximation at 0 K with an applied field H_z in the z direction reduces to

$$F/M_0=-H_E+H_E'(-\sigma_{1y}^2+\sigma_{1z}^2)+H_{A2}\sigma_{1z}^2-2H_d\sigma_{1y}\sigma_{1z}-g_cH_z\sigma_{1z}, \tag{1}$$

where H_E, H_E', H_{A2}, and H_d are the intralayer and interlayer interaction parameters, the intralayer anisotropy parameter in the y-z plane, and the antisymmetric anisotropy parameter, respectively; $\vec{\sigma}$ is the reduced spin $\vec{S}/S$ and $g_c=2g_{zz}/g_{xx}=1.956$. (We use for the g-tensor components g_{xx} and g_{zz} the values measured by Vega and Maarschall.[27]) In accordance with the definition in Ref. 5 we use for M_0 the sublattice saturation magnetization per unit volume: $M_0=2Sg_{xx}\mu_B/a_0b_0c_0$, where μ_B is the Bohr magneton and a_0, b_0, and c_0 are the dimensions of the unit cell. As discussed in Ref. 5 we can neglect the interlayer antisymmetric parameter because it is expected to be relatively small. The part of the interlayer anisotropy originating from the exchange interaction will be very small; the part originating from dipole-dipole interaction is of the order of 100 Oe[4,5] and will be neglected. If α is the angle between the magnetic moments of sublattice 1 and the y axis and of the moments of sublattice 2 and the negative y axis [Fig. 4(a)] we can write expression (1) as

$$F/M_0=-H_E+\tfrac{1}{2}H_{A2}-(H_E'+\tfrac{1}{2}H_{A2})\cos 2\alpha-H_d\sin 2\alpha-g_cH_z\sin\alpha. \tag{2}$$

The angle α can be derived from the measured magnetization M versus applied field curve (Fig. 2). The samples are flat platelets, hence the demagnetization factor equals 4π. From the slope of the M vs H curve it follows that $4\pi M_s=130\pm15$ Oe, where M_s is the magnetization of the domains per unit volume. (In fact the M_s so obtained is still a function of temperature and has been extrapolated to $T=0$ K.) This should be compared with the saturation magnetization, 320 Oe, which can be calculated from the dimensions of the unit cell. This gives $\alpha=24\pm3°$. Magnetic torsion balance measurements of Bloembergen *et al.*[26] on $(C_3H_7NH_3)_2CuBr_4$ give an estimated $H_E'=2.5$ kOe and $H_{A2}=1.2$ kOe. Using these values of H_E' and H_{A2} and $\alpha=24°$ we find by minimizing (2) $H_d=3.4$ kOe.

From the other three allowed magnetic structures only the *Pb′ca′* structure has a free energy comparable with the free energy of the *Pb′c′a* structure [Fig. 4(b)]. The spin components for the *Pb′ca′* structure are

$$S_{1x}=S_{2x}=0;\quad S_{1y}=S_{2y};\quad S_{1z}=-S_{2z}.$$

The expression for the free energy at 0 K and zero applied field becomes

$$\begin{aligned}F/M_0&=-H_E+H_E'(\sigma_{1y}^2-\sigma_{1z}^2)+H_{A2}\sigma_{1z}^2-2H_d\sigma_{1y}\sigma_{1z}\\&=-H_E+\tfrac{1}{2}H_{A_2}+(H_E'-\tfrac{1}{2}H_{A2})\cos 2\beta-H_d\sin 2\beta,\end{aligned}$$

where β is the angle between the spin moments and the y axis. The free energy has a minimum for $\tan 2\beta=-H_d/(H_E'-\frac{1}{2}H_{A2})$; for this angle of β we find that $E_2\equiv F/M_0+H_E$ (for $45°\leqslant\beta\leqslant 90°$):

$$E_2=\tfrac{1}{2}H_{A2}-[(H_E'-\tfrac{1}{2}H_{A2})^2+H_d^2]^{1/2}. \tag{3}$$

If we compare E_2 with the analogous quantity for the *Pb′c′a* structure, E_1, using the above given values of H_{A2}, H_E', and H_d, we find $E_1=-4.0$ kOe and $E_2=-3.3$ kOe. This shows that a relatively small change in one or more of the interaction parameters can make the *Pb′ca′* structure the most favorable structure.

To discuss the type B crystals we have to consider the possible structures in the presence of a magnetic field along the c axis. Group-theoretical arguments[28] show that also in the case of an applied field along the c axis four different magnetic structures are possible. In the limit of zero field these structures should correspond to the four zero field structures. In this way we find that the in-field structure $S_{1x}=S_{2x}=0; S_{1y}=-S_{2y}$, and $S_{1z}=S_{2z}$ corresponds to the *Pb′c′a* structure while $S_{1x}=S_{2x}=0$ and arbitrary values of S_{1y}, S_{2y}, S_{1z}, and S_{2z}, corresponds to the *Pb′ca′* structure (Fig. 4). We can explain the observed behavior of the type B crystals if we assume that the interaction parameters of type B are such that the *Pb′ca′* structure has a slightly lower free energy in zero field than the *Pb′c′a* structure. A magnetic field along the z direction will in first order not change the free energy of the *Pb′ca′* structure while for the *Pb′c′a* structure the field-dependent part of the free energy changes approximately proportional with field.

This means that a critical field H_c exists at which a field induced first-order phase transition from the *Pb'ca'* to the *Pb'c'a* structure begins to occur locally. Demagnetizing fields prevent the spreading of the *Pb'c'a* structure over the whole sample. There is a field interval (coexistence region) above H_c where domains of *Pb'c'a* structure and *Pb'ca'* structure alternate while the internal field is kept at 215 Oe due to the demagnetizing fields. In the coexistence region we have a relation between H and M analogous to the relation for a simple (weak) ferromagnet: $\Delta H = 4\pi\Delta M$. From the measurements (Fig. 2) it follows that for the weak ferromagnetic moment of the *Pb'c'a* domains: $4\pi M_S = 120 \pm 10$ Oe. This gives $\alpha = 22°$ in an internal field of 215 Oe. In the case of the type-B crystals the information from the experiment ($H_c = 215$ Oe, $\alpha = 22°$) is not sufficient to solve the three unknown parameters H'_E, H_{A2}, and H_d. However, we can deduce some relations between the parameters.

Minimization of (2) gives

$$H_d = (H'_E + \tfrac{1}{2}H_{A2})\tan 2\alpha - g_c H_z(\cos\alpha / 2\cos 2\alpha). \quad (4)$$

For $\alpha = 22°$ and $H_z = 215$ Oe this becomes

$$H_d = 0.97(H'_E + \tfrac{1}{2}H_{A2}) - 270. \quad (5)$$

Substituting the above expression (4) for H_d in the expression for E_1 (2) and E_2 (3) and using $E_1 = E_2$ at $H_z = H_c$, one can express H_{A2} in terms of H'_E:

$$H_{A2} = \frac{\frac{1}{4}H_c^2 g_c^2(1 + \sin^2\alpha + 2\sin^4\alpha) - 2g_c H_c H'_E \sin\alpha}{g_c H_c \sin\alpha + 2H'_E \cos 2\alpha}.$$

For $\alpha = 22°$ and $H_c = 215$ Oe this becomes

$$H_{A2} = 219\,\frac{166 - H'_E}{109 + H'_E}\ \text{Oe}. \quad (6)$$

As stated above we can not determine H_{A2}, H_d, and H'_E, however, if the H'_E for type B is of the same order of magnitude as for type A then it follows from (5) and (6) that approximately $H_{A2} \approx -200$ Oe and $H_d \approx 0.97H'_E - 400$ Oe. Because of the approximations involved we have to consider the obtained numerical values more as estimates than as precise results.

It is not uncommon for substances with two-dimensional magnetic interactions to exhibit different magnetic structures. Gurewitz *et al.*[29] found different structures in Rb_2MnCl_4 depending on the preparation method of the samples. Birgeneau *et al.*[30] observed two structures in samples of $RbMnF_4$. It is not surprising that the two-dimensional magnetic compounds are likely candidates for this magnetic polytypy. As mentioned in Refs. 29 and 31 the three-dimensional ordered structure is determined by the combined influence of a number of interaction and anisotropy fields which all are very small compared with the interlayer interaction but can be mutually of comparable magnitude. In such a situation a small change in the properties of the material caused for example by a different preparation method ($RbMnCl_4$), different amount of impurities and dislocations, stress, or different crystal structure, can easily change the balance of interaction and anisotropy fields in such a way that a different magnetic structure becomes the most favorable.

CONCLUSION

At liquid-helium temperatures there exist two magnetic modifications (type A and type B) in $(C_3H_7NH_3)_2CuBr_4$ crystals. Crystals (or parts of crystals) exhibiting type-A behavior have gone through a structural phase transition below 90 K, while the crystals showing type-B behavior have not. Cooling speed, crystal perfection, stress and crystal size are decisive factors in inducing the possible structural phase transition. Especially, both the experiments of de Jongh[25] as well as our own observations, indicate that the size of the crystals plays an important role.

The magnetic properties of type-A crystals below the magnetic transition temperature can be described by the weak ferromagnetic *Pb'c'a* structure consisting of antiferromagnetic coupled ferromagnetic copper bromine layers with an angle α between the spins and the xy plane equal to 24 ± 3°, leading to a net ferromagnetic moment. Combining our experimental data with the torsion balance measurements of Bloembergen[26] we find for the antisymmetric anisotropy parameter $H_d = 3.4$ kOe.

The type-B crystals show domains for fields between 215 Oe and 350 Oe. This can be explained by assuming a magnetic *Pb'ca'* structure in zero field. At an applied field of 215 Oe or larger the *Pb'c'a* structure becomes energetically more favorable and a first-order phase transition to this structure sets in. Between 215 and 350 Oe there coexist alternating domains of the *Pb'c'a* and *Pb'ca'* structure. At 350 Oe the single domain state is reached. A comparable situation has been observed in MnF_2.[13,32] Therein is a small field range (92.4 to 92.9 kOe) above the spin-flop field, where domains of spin-flopped and nonspin-flopped structure coexist.

ACKNOWLEDGMENTS

We would like to thank Professor A. R. Miedema for the suggestion of this problem. We are indebted to Dr. P. Bloembergen and Dr. L. J. de Jongh for making available results prior to publication and for many enlightening discussions, to Dr.

Th. W. J. Janssen for solving a group-theoretical problem, and to Dr. P. Bennema for his stimulating interest.

This work was performed as part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) with financial support from the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (ZWO).

---

*Permanent address: Laboratory of Physical Chemistry, Delft University of Technology, Delft, The Netherlands.

[1] A. R. Miedema, J. Phys. C 32, C1-305 Suppl. Met. Phys. (1971).

[2] P. Bloembergen, K. G. Tan, F. H. J. Lefèvre, and A. H. M. Bleyendaal, J. Phys. C 32, C1-878 Suppl. Met. Phys. (1971).

[3] L. J. de Jongh, W. D. van Amstel, and A. R. Miedema, Physica 58, 277 (1972).

[4] J. H. P. Colpa, Physica 57, 347 (1972).

[5] P. Bloembergen, P. J. Berkhout, and J. J. M. Franse, Int. J. Magn. 4, 219 (1973).

[6] R. D. Willet and J. P. Steadman, Inorg. Chim. Acta 4, 367 (1970).

[7] F. Barendregt and H. Schenk, Physica 49, 465 (1970).

[8] A. R. Kop, see private communication in Ref. 4; A. Daoud, thesis (University of Dyon, France, 1976) (unpublished).

[9] N. D. Mermin and H. Wagner, Phys. Rev. Lett. 17, 1133 (1966).

[10] H. van Kempen, F. H. Mischgofsky, and P. Wyder, in *Proceedings of the Twelfth International Conference on Low Temperature Physics*, edited by E. Kanda (Academic Press of Japan, Tokyo, 1971), p. 811.

[11] H. van Kempen, F. H. Mischgofsky, and P. Wyder, Rev. Sci. Instrum. 43, 1209 (1972).

[12] Philips image intensifier OB 120 with a S25 photocathode.

[13] K. L. Dudko, V. V. Eremko, and V. M. Fridman, Zh. Eksp. Teor. Fiz. 61, 1553 (1971) [Sov. Phys.-JETP 34, 828 (1972)].

[14] H. Arend, R. Hofmann, and J. Felsche, Ferroelectrics 8, 413 (1974).

[15] K. Knorr, I. R. Jahn, and G. Heger, Solid State Comm. 15, 231 (1974).

[16] J. Petzelt, J. Phys. Chem. Solids 36, 1005 (1975).

[17] R. Kind and J. Roos, Phys. Rev. B 13, 45 (1976).

[18] G. Chapuis, H. Arend, and R. Kind, Phys. Status Solidi A 31, 449 (1975).

[19] D. Brinkmann, U. Walther, and H. Arend, Solid State Commun. 18, 1307 (1976).

[20] W. Depmeier, J. Felsche, and G. Wildermuth (unpublished).

[21] G. Chapuis and J. L. Gloor, in Third European Crystallographic Meeting (Zürich), Collected Abstracts, 1976 (unpublished), p. 126.

[22] H. Arend, F. H. Mischgofsky, and F. Tuinstra (unpublished).

[23] J. Holvast, J. H. M. Stoelinga, and P. Wyder, Ferroelectrics 13, 543 (1976).

[24] J. H. M. Stoelinga and P. Wyder, J. Chem. Phys. 64, 4612 (1976).

[25] L. J. de Jongh (private communication).

[26] P. Bloembergen (private communication).

[27] See private communication in Ref. 4.

[28] Th. W. J. Janssen (private communication).

[29] E. Gurewitz, A. Epstein, J. Makovsky, and H. Shaked, Phys. Rev. Lett. 25, 1713 (1970).

[30] R. J. Birgeneau, H. J. Guggenheim, and G. Shirane, Phys. Rev. B 1, 2211 (1970).

[31] W. D. van Amstel and L. J. de Jongh, Solid State Comm. 11, 1423 (1972).

[32] A. R. King and D. Paquette, Phys. Rev. Lett. 30, 662 (1973).

FIG. 1. Domains in zero applied field in type-*A* crystals at $T = 2$ K. The contrast is enhanced by photographic methods.

FIG. 3. Domains in a type-*B* crystal in an applied field of 280 Oe at $T = 2$ K.