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The Magnetic Properties of the High Pressure Phase of Ferric Phosphate, $FePO_4$-II

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$FePO_4$-II has been prepared by treating berlinite-like $FePO_4$-I at 850°C and 4 GPa. The high pressure phase is isostructural with the orthorhombic, divalent sulfates MSO_4 (M = Mn, Fe, Co, and Ni) and thus contains chains of 6-coordinate Fe^{3+} ions. Susceptibility and Mössbauer measurements indicate that $FePO_4$-II is antiferromagnetically ordered at 4.2 K. Weak interchain coupling leads to the observation of relaxation phenomena in the Mössbauer spectra between 43 K and the magnetic ordering temperature of ca. 60 K. A model which can account for these observations is proposed for the magnetic structure; it consists of weakly ferromagnetic [001] chains, coupled together antiferromagnetically. © 1986 Academic Press, Inc.

Introduction

The antiferromagnetic behaviour of transition metal acid salts has been studied extensively over a period of many years. One aim of the research has been to determine the sensitivity of the low-temperature magnetic structure to the *d*-electron configuration of the metal ion, and the isostructural series $MnSO_4$, $FeSO_4$, $CoSO_4$, and $NiSO_4$ has consequently been the subject of many investigations (*1*, *2*). The crystal structure of all these materials (Fig. 1) consists of infinite chains of trans-edge sharing MO_6 octahedra parallel to [001] with SO_4 tetrahedra linking the chains, and thus two distinct magnetic interactions take place; an intrachain superexchange along a short M–O–M pathway and an interchain interaction along a longer M–O–S–O–M pathway. The relative strength of these two interactions, itself partly determined by electron configuration, determines the type of magnetic ordering which is found below the Néel temperature, and it has been established that many different types can occur. $FeSO_4$ and $NiSO_4$ have simple colinear magnetic structures whereas $CoSO_4$ has a rather more complex coplanar spin structure that can be thought of as a combination of two different colinear structures (*1*). The antiferromagnetic phase of $MnSO_4$ (*2*) is even more complex with the magnetic moments being arranged in a cycloidal spiral. The

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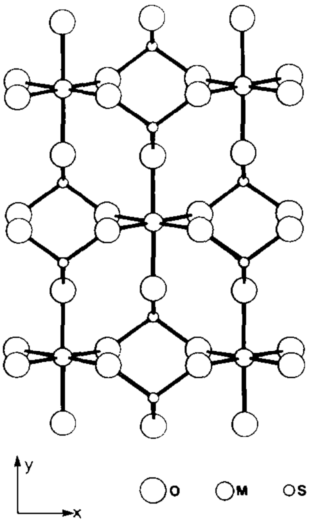

FIG. 1. The crystal structure of $M^{2+}SO_4$ projected on (001) (M = Mn, Fe, Co, Ni).

magnitudes of the superexchange interactions are clearly very sensitive to the number of 3*d* electrons associated with the transition metal ion.

A number of materials have been synthesized in attempts to extend the range of acid salts studied to include those of the trivalent cations Fe^{3+} and Cr^{3+}, using VO_4^{3-} or PO_4^{3-} as counterions. $CrVO_4$ and β-$CrPO_4$ are both isostructural with the divalent sulfates but they adopt different magnetic structures below their Néel temperatures; $CrVO_4$ has a colinear magnetic structure (*1*) whereas β-$CrPO_4$ (*3*) has an incommensurate cycloidal spiral structure, thus demonstrating the dependence of magnetic properties on the counter ion. Unfortunately neither $FeVO_4$ nor $FePO_4$ is of the same structural type as the divalent sulfates when prepared at atmospheric pressure, but $FePO_4$ does transform from its quartz-like structure when subjected to high pressure (*4*).

Before we move on to describe the magnetic properties of the high pressure phase $FePO_4$-II, it will be useful to review the structural and magnetic properties of $FePO_4$-I, the low pressure phase. $FePO_4$-I is isostructural with the mineral berlinite ($AlPO_4$), and the crystal structure thus consists of an infinite network of FeO_4 and PO_4 tetrahedra, linked together by corner sharing (*5*). The material has a Néel temperature of $T_N \sim 25$ K and it undergoes an unusual spin-reorientation transition at ~17 K (*6*). The antiferromagnetic phase of $FePO_4$-I has been well characterized by neutron diffraction, Mössbauer spectroscopy, and magnetic susceptibility measurements (*6*). Kinomura *et al.* (*4*) have shown that the application of a 50 kb pressure at 900°C converts the berlinite-like phase to $FePO_4$-II which is apparently isostructural with the divalent metal sulfates discussed above. The transformation, involving a change in coordination number of the Fe^{3+} ions from 4 to 6, is accompanied by a dramatic (22.6%) increase in density. Room temperature Mössbauer spectra and susceptibility measurements made between 80 K and room temperature indicated that the high pressure phase contains high spin Fe^{3+} ions in a somewhat distorted octahedral environment. In this paper we report an investigation of the low temperature magnetic properties of $FePO_4$-II, performed by Mössbauer spectroscopy and magnetic susceptibility measurements. Our results serve to illustrate the dependence of magnetic properties on structure for the two isomorphs of $FePO_4$, and also to reveal yet another type of magnetic ordering in the series of orthorhombic acid salts MXO_4.

Experimental

Attempts, following Kinomura *et al.* (*4*), to prepared $FePO_4$-I by precipitation methods from aqueous solution yielded materials contaminated by other phases. Satisfactory preparation of $FePO_4$-I was achieved by slowly heating a stoichiometric mixture of Fe_2O_3 and $(NH_4)_2HPO_4$ to 900°C. The temperature was held at this level for 24 hr before the product was quenched to room temperature. Chemical analysis found 36.85% Fe and 20.85% P in the sample (calcd for $FePO_4$; 37.0% Fe, 20.55% P) and X-ray powder diffraction established that $FePO_4$-I was the only crystalline phase present (*5*).

Samples of about 45 mm^3, packed in thin-walled platinum tubes of 3.76 mm diameter with platinum end plugs, were subjected to high pressure and temperature conditions in a conical double-piston apparatus (*7*). After heating to 850°C at 4 Gpa for 2 hr, the samples were cooled under pressure. The product was ground and the high pressure form (ρ = 3.90 g cm^{-3}) separated from any remaining amounts of the low pressure form (ρ = 3.02 g cm^{-3}) by centrifugation in diiodo methane (ρ = 3.325 g cm^{-3}). The dense solid was washed with cyclohexane and dried in air. All the lines in the X-ray powder pattern of this material could be indexed with an orthorhombic unit cell having a = 5.28(4), b = 7.79(3), and c = 6.34(3) Å, in reasonable agreement with the unit cell proposed by Kinomura *et al.* (*4*) for Fe PO_4-II.

The magnetic susceptibility of $FePO_4$-II was measured in the temperature range 4.2 $< T <$ 90 K using an Oxford Instruments Faraday balance operating with an applied field of 9.95 kG and a field gradient of 122 G cm^{-1}. Mössbauer spectra were recorded for absorber temperatures in the range 4.2 $< T <$ 300 K with a $^{57}Co/Rh$ source matrix at room temperature; isomer shift values are relative to the spectrum of metallic iron. Temperatures below 80 K were obtained using liquid helium in an Oxford Instruments CF500 Continuous Flow Cryostat controlled by a DTC2 Digital Temperature Controller. The main spectrometer was based upon an MS-102 Microprocesser by Cryophysics Ltd. All data were computer-fitted.

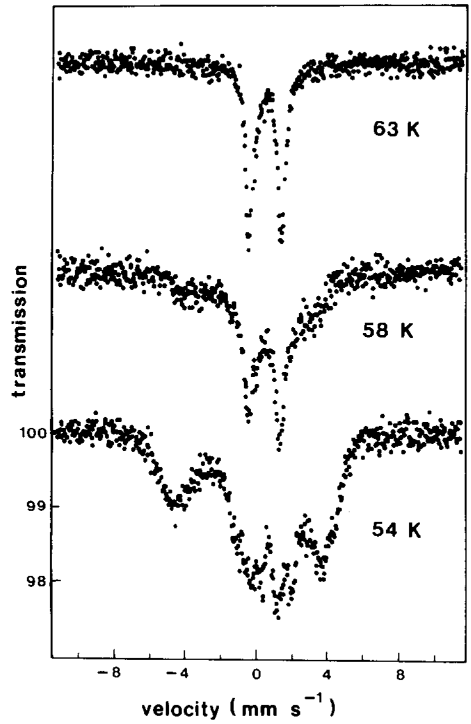

FIG. 2. Selected Mössbauer spectra of $FePO_4$-II in the temperature range $54 \leq T \leq 63$ K.

Results and Discussion

Selected Mössbauer spectra measured in the temperature range $4.2 < T < 63$ K are shown in Figs. 2 and 3. At 63 K the spectrum comprises a simple, symmetrical quadrupole doublet with a chemical shift of +0.539 ± 0.010 mm s^{-1}, which is typical of 6-coordinate high spin Fe^{3+} ions. The quadrupole splitting is Δ = 1.811 ± 0.010 mm s^{-1}, a relatively large value for a $^6A_{1g}$: Fe^{3+} ion, thus indicating that there is a considerable distortion away from perfect octahedral coordination around the Fe^{3+} site. Below ca. 60 K the spectrum changes to a six-line pattern due to the onset of long-range magnetic order. The spectrum at 4.2 K comprises a single, asymmetric magnetic pattern, and thus indicates that the internal hyperfine field and the principal axis of the

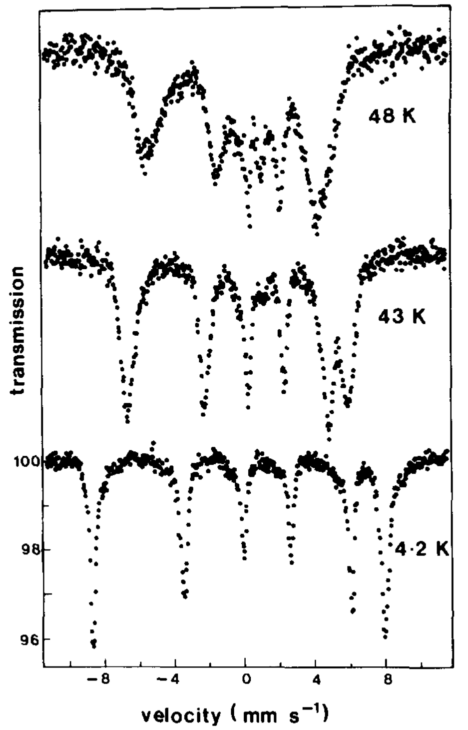

FIG. 3. Selected Mössbauer spectra of FePO$_4$-II in the temperature range $4.2 \leq T \leq 48$ K.

electric field gradient (efg) tensor are in the same relative orientation at all the Fe^{3+} sites in the unit cell.

The asymmetry in the 4.2 K spectrum arises from the quadrupole interaction acting as a perturbation upon the magnetic interaction, and it contains information regarding their relative orientation. The principal axis of the magnetic field, and hence the spin axis at a particular site, can be defined with respect to the principal axis system, xyz, of the efg tensor by the polar angles θ and ϕ. The tensor is conventionally expressed in the principal axis system by the quadrupole coupling constant $e^2qQ \equiv eQV_{zz}$ (where Q is the nuclear quadrupole moment) and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ such that $0 \leq \eta \leq 1$. A single six-line spectrum from a randomly orientated powder sample does not contain enough information to determine e^2qQ, θ, ϕ, and η unambiguously, but it does provide some restriction on the ranges of allowed values for these parameters. A detailed discussion of these restrictions has been given by Le Caër *et al.* (*8*) and their conclusions are used in the following discussion. If the six lines of the hyperfine pattern are numbered from 1 to 6, from negative to positive velocities, then the difference in the separation of the outer lines is $4\varepsilon = (V_6 - V_5) - (V_2 - V_1)$ where ε expresses the quadrupole perturbation to first order and can be written as

$$\varepsilon = \tfrac{1}{8}e^2qQ(3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\phi).$$

The experimental value at 4.2 K is $\varepsilon = -0.834 \pm 0.003$ mm s^{-1} with a chemical shift of 0.53 mm s^{-1} and a field value of $H = 516.5 \pm 0.1$ kG. Le Caër *et al.* define the ratio $R = 2\varepsilon/\Delta$, and bearing in mind that the sign of Δ $(=(e^2qQ/2)(1 + \eta^2/3)^{1/2})$ is unknown, our data yield a value for $|R|$ of 0.92 ± 0.01. In obtaining this value of $|R|$ it has been assumed that the quadrupole interaction remains essentially unchanged in the magnetic phase. From the published graphs (*8*) it is clear that the lower limit for R is -0.866, so that in our case R must be positive, hence Δ is negative and e^2qQ is also negative. Furthermore, the parameters describing the orientation of the internal hyperfine field and the principal axis, z of the efg tensor are restricted to a range between $\theta = 0$, $\eta = 0.7$, and $\theta = 13°$, $\eta = 0$, while ϕ remains effectively undefined. Thus we reach the important conclusion that the spin axis lies within 13° of the principal axis of the efg tensor, and $\eta \leq 0.7$.

The efg tensor in the paramagnetic phase must follow the symmetry restrictions imposed by the $2/m$ point symmetry of the Fe^{3+} site in the orthorhombic crystal structure (4*a* site, space group *Cmcm*), and even if the magnetic space group has a lower symmetry it is unlikely to have any significant influence on the electric field gradient. Consequently, one of the principal axes xyz must lie along the crystallographic a axis, while the other pair are in the bc plane. Similarly, the spin axis must lie along a or in the bc plane unless the magnetic symmetry has been lowered. It is therefore possible that either the spin axis is collinear with V_{zz} and lies along a, or the spin axis and V_{zz} are in the bc plane and less than 13° apart. It has proved difficult to reconcile the former with the point charge calculations described below, and with the relaxation behavior found above 40 K and described later in the paper.

Although the atomic coordinates are not known accurately for $FePO_4$-II, they are available for the isostructural compound β-$CrPO_4$ (*3*). A point charge calculation of the efg tensor at the Fe^{3+} site was made using this structural data. The charge on the cation was fixed at +3, and the overall charge on the anion at −3, but the nominal charge on the phosphorus was varied in steps from 0 to +5. The results proved to be surprisingly informative. The sign of e^2qQ remains negative, as required, for charges on the phosphorus between +1.1 and +5, while V_{zz} remains in the bc plane and is never more than 13° from the b axis; V_{zz} never lies along the a axis. These calculations provide strong evidence in favour of a model in which the spin axis and V_{zz} are in the bc plane and close to the b axis.

The Mössbauer spectrum at 4.2 K shows slight asymmetry in the wings of the hyperfine lines which is consistent with the presence of a small contamination (<5%) by the low pressure phase $FePO_4$-I. The latter has been shown (*6*) to have parameters of H = 511 kG, δ = 0.45 mm s^{-1}, and ε = −0.15 mm s^{-1} at 4.2 K and the computed line positions are consistent with the observed asymmetry. Evidence for a second phase was also found in the room temperature Mössbauer spectrum. The Néel temperature of $FePO_4$-I is only 25 K, so that the weak additional absorption in the center of the spectrum at 43 K can be attributed to a quadrupole doublet from this phase. The decrease in isomer shift to 0.45 mm s^{-1} for $FePO_4$-I, in which the Fe^{3+} ions are 4-coordinated, compared to 0.53 mm s^{-1} for $FePO_4$-II, in which the Fe^{3+}-ions are 6-coordinated, is as expected. However, one would usually expect that the internal magnetic field for 4-coordination would be significantly smaller than that for 6-coordination, whereas the experimentally observed values are almost identical. A possible explanation for this will be given later.

In the Mössbauer spectra recorded above 40 K there is a progressive increase in the broadening of the outer lines of the spectrum and an increase in intensity in the center of the spectrum which is typical of relaxation behavior. There is no evidence for a major change in spin axis. The internal magnetic field decreases in a Brillouin behavior between 4.2 and 40 K but becomes difficult to follow above 50 K and the magnetic ordering temperature can only be estimated as ca. 60 K. The onset of relaxation well below this temperature suggests an anisotropic superexchange interaction, and it is significant to note that similar relaxation has been observed in the near one-dimensional antiferromagnetic K_2FeF_5 which also contains chains of Fe^{3+} ions (*9*).

The inverse molar magnetic susceptibility of $FePO_4$-II is plotted as a function of temperature in Fig. 4. Above ca. 60 K the data appear to follow a Curie–Weiss law, although our results do not extend to high enough temperatures to permit the calculation of a meaningful Weiss constant, θ, or effective magnetic moment. The shape of the $1/\chi : T$ curve suggests that the material is weakly ferromagnetic immediately below the magnetic ordering temperature, transforming to an antiferromagnetic phase below ca. 43 K. The observation of unusual effects in both the Mössbauer spectra and

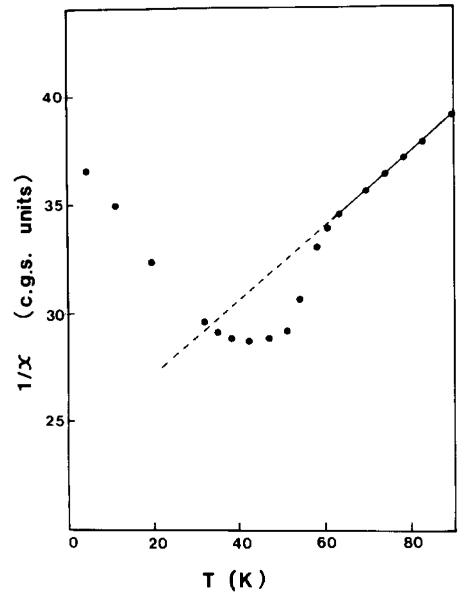

FIG. 4. The inverse molar magnetic susceptibility of $FePO_4$-II as a function of temperature below 90 K.

the magnetic susceptibility in the temperature range 40 < T < 60 K suggests that there may be a common cause linked to the highly anisotropic exchange interactions in the structure.

All of our observations can be accounted for by the magnetic structure illustrated in Fig. 5. The Fe^{3+} sites at (0,0,0) and $(0,0,\frac{1}{2})$ are related by a 2_1 screw axis, as are those at $(\frac{1}{2}\frac{1}{2}0)$ and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, and the site at (0,0,0) is identical to that at $(\frac{1}{2}\frac{1}{2}0)$. The proposed spin arrangement thus ensures that the angle between the principal axis and the internal hyperfine field is identical at every Fe^{3+} ion site. The spin axis is aligned in the bc plane close to the b axis, and hence close to V_{zz}. Ferrimagnetic coupling of the spins along a c axis chain results in a cancellation of the magnetic moments parallel to b, but leaves a small ferromagnetic component along c, as indicated by the thick arrows in Fig. 5. Antiferromagnetic coupling between the spins at $(\frac{1}{2}\frac{1}{2}0)$ and (000) ensures that the ferromagnetic components of neighboring chains cancel, and the overall behaviour is antiferromagnetic as observed. As the coupling between chains is expected to be weak, the magnetic field applied during the susceptibility measurement may cause the weak ferromagnetic components of the individual chains to align in a common direction, thus inducing a weak ferromagnetism, close to the ordering temperature. Such an effect could not be produced if the spins were to lie along the a axis.

The model we propose for the magnetic structure of $FePO_4$-II is similar to the coplanar structure proposed for $CoSO_4$ by Frazer and Brown (Fig. 6) the most striking difference being that they found the ferromagnetic component of each chain to lie along the b-axis rather than along c. Such a model requires essentially ferromagnetic coupling along the [001] chains whereas our model has essentially antiferromagnetic coupling

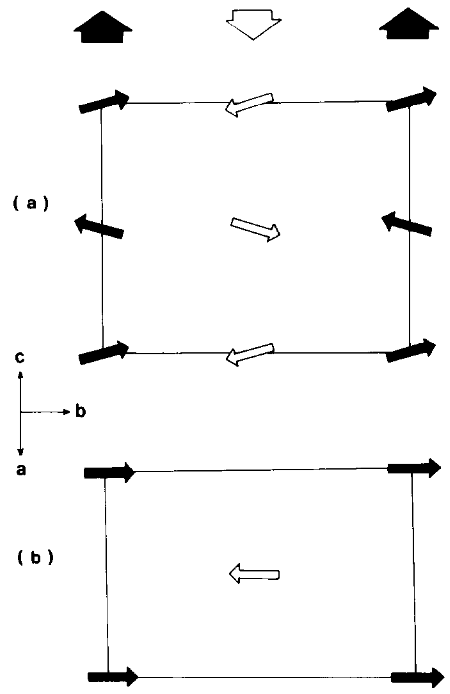

FIG. 5. The magnetic structure proposed for $FePO_4$-II, (a) projected on the bc plane and (b) in the ab plane, c = 0.

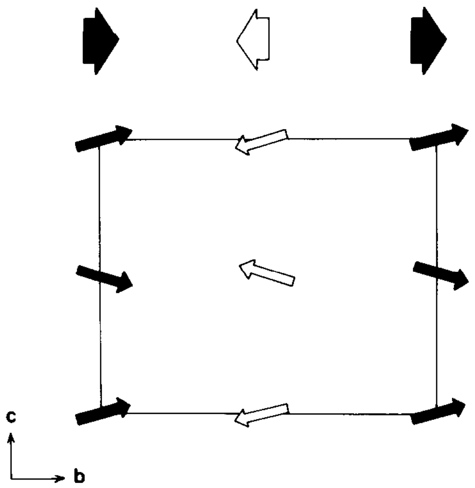

FIG. 6. The magnetic structure of $CoSO_4$ (after Frazer and Brown).

in that direction. The latter seems more likely in $FePO_4$-II because the superexchange between the half-filled t_{2g} orbitals of Fe^{3+} ions in edge-sharing octahedra is expected to be strongly antiferromagnetic (*10*). This is entirely consistent with the magnetic structures of $CrVO_4$ (*1*), β-$CrPO_4$ (*6*), $MnSO_4$ (*2*), and $MnSeO_4$ (*11*), all of which have antiferromagnetic coupling along [001] chains of cations with half-filled t_{2g} orbitals. Ferromagnetic coupling along the chains is only observed when the t_{2g} orbitals are more than half-filled, $NiSO_4$ (*1*) being the extreme case. However, we emphasize that our experimental data do not allow us to dismiss the possibility that $FePO_4$-II and $CoSO_4$ are magnetically isostructural. Our preference for the magnetic structure illustrated in Fig. 5 is based on theoretical predictions of the relative strength of the antiferromagnetic and ferromagnetic coupling along the chains of edge-sharing octahedra. We believe this to be the only model which explains all the observed phenomena and satisfies theoretical predictions without imposing restrictions on either the spin direction or the principal axis of the efg tensor, other than those required by the $2/m$ point symmetry of the cation site. Neutron diffraction would, of course, resolve the matter unambiguously, but such experiments are not at present possible using the small amount of sample produced in a high pressure synthesis. As Frazer and Brown (*1*) themselves point out, symmetry does not require $NiSO_4$ and $FeSO_4$ to have colinear spin structures, and it is possible that these materials also possess a weak ferromagnetic component, too small to be detected in neutron diffraction experiments on polycrystalline samples.

The relatively weak interchain coupling is probably responsible for the internal magnetic field being almost identical at 4.2 K in both forms of $FePO_4$. The one-dimensional magnet K_2FeF_5 shows an exceptionally small saturation hyperfine field of 410 kG compared to 618 kG in FeF_3 (*9*). This large zero-point spin reduction is characteristic of one-dimensional systems, having been observed previously in $CsMnBr_3$, $CsNiCl_3$, and $KCuF_3$. The reduction in the saturation hyperfine field in $FePO_4$-II is unlikely to be more than 30–40 kG, which demonstrates that the exchange anisotropy is far less extreme than in K_2FeF_5. However, the strength of the superexchange interactions between Fe^{3+} ions in edge-sharing octahedral sites is demonstrated by the relatively high magnetic ordering temperature of ~60 K, which can be compared to 25 K for $FePO_4$-I and 4 K for $KBaFe_2(PO_4)_3$ (*12*), the latter compound consisting of FeO_6 octahedra linked only by corner-sharing phosphate groups. Furthermore, $FePO_4$-II has a higher Néel temperature than any other MXO_4 compound studied to date (*1, 3, 10*), an observation whose explanation must lie in the as yet unknown details of the crystal and electronic structure.

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