Investigation of magnetic properties of a crystal of superionic conductor $Li_3Fe_2(PO_4)_3$

A. B. Bykov, T. M. Perekalina, E. M. Smirnovskaya, V. G. Terziev, V. A. Timofeeva, and S. A. Cherkezyan

A. V. Shubnikov Institute of Crystallography, Academy of Sciences of the USSR, Moscow

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A study was made of the magnetic properties of a crystal of the superionic conductor $Li_3Fe_2(PO_4)_3$. The measured magnetic susceptibility was found to obey the Curie-Weiss law. An induced unidirectional magnetic anisotropy with a rotational hysteresis was observed. Two possible explanations of the observed anisotropy were considered and its disappearance was probably associated with a transition of the crystal to the superionic state.

Orthorhombic crystals of $Li_3Fe_2(PO_4)_3$, which is a superionic conductor above 518 K, were grown from a molten solution using a $LiF–Fe_2O_3–P_2O_5–V_2O_5$ mixture and a seed attached to a platinum rod rotating in the solution.[1] Crystallization took place in the temperature interval 800–650°C at a cooling rate of about 1°C/h. The conductivity of these crystals was due to lithium ions.[2]

We selected the largest (up to 500 mg) crystals in the magnetic investigation. According to the Mössbauer data, these crystals contained an Fe_2O_3 impurity. Smaller crystals (30 mg) were free of this impurity, but they were too small to ensure a satisfactory accuracy in our measurements.

We shall report below the results of a study of the magnetic properties of a crystal of the investigated compounds in relation to its superionic conduction.

The magnetic susceptibility of $Li_3Fe_2(PO_4)_3$ was investigated in the temperature range 290–600 K using magnetic fields up to 20 kOe. The susceptibility was determined by the usual magnetic-balance method and the magnetic anisotropy was determined in the temperature range 77–600 K by the torque method with an error up to ± 20 erg/g. The magnetization and its temperature dependence were studied in the range 4.2–300 K by the vibration-magnetometer method in a superconducting solenoid made by PAR (USA) with an error up to $0.01\ G \cdot cm^3 \cdot g^{-1}$. A preliminary study was made of the Mössbauer spectra. The data on the magnetic susceptibility χ showed that the Curie-Weiss law $\chi = C/(T-70)$ was obeyed in the temperature range 290–600 K.

The magnetic anisotropy of $Li_3Fe_2(PO_4)_3$ was determined by two methods. In the first we used the conventional technique. It involved determination of the torque L when the crystal was rotated in a magnetic field. The torque curve $L(\vartheta)$ obtained at 77 K in a field of 10 kOe is denoted by 1 (clockwise rotation) and 2 (anticlockwise rotation) in Fig. 1. The anisotropy was independent of the crystallographic plane in which measurements were carried out. Any direction of ϑ_0 in a crystal along which the magnetic field was applied became its magnetic anisotropy axis ($\vartheta_0 = 0$ in Fig. 1). Before the application of the field the crystal should be heated above the superionic transition temperature and cooled to a given temperature below this transition. Otherwise the magnetic anisotropy induced by the previous field was not eliminated completely. It is clear from Fig. 1 that the curves recorded by the first technique were different for the clockwise and counterclockwise directions. Curve 1 was entirely in the negative part of $L(\vartheta)$, whereas curve 2 was in the positive part. This behavior of $L(\vartheta)$ indicated that in the course of rotation of the crystal in the magnetic field its anisotropy axis varied and curves 1 and 2 could not be used to distinguish the uniaxial from the unidirectional or any other anisotropy. The nature of the anisotropy was determined by the second method. In this method a field of up to 20 kOe intensity was applied along some direction ϑ_0 ($\vartheta_0 = 0$ in Fig. 1) and then switched off. The field was applied next along a different direction in the crystal $\vartheta = \vartheta_0 + \varphi$, and the torque was measured as a function of the field: $-L(H)$. In this case the new anisotropy induced along the $\vartheta_0 + \varphi$ direction gave rise to zero torque in this $\vartheta_0 + \varphi$ direction. However, the measured torque was due to the anisotropy induced by the field along ϑ_0. The inset in Fig. 1 gives, by way of example, the $L(H)$ curve obtained for $\varphi = \pi/2$. We used 36 such dependences, recorded in steps of ten angular degrees, to plot

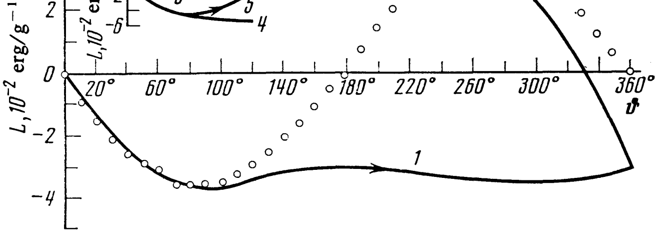

FIG. 1. Torque curves obtained for $Li_3Fe_2(PO_4)_3$ at 77 K in a field of 10 kOe: method 1 (curves 1 and 2) and method 2 (curve 3). The inset shows the field dependences of the torque $L(H)$: curve 4 was obtained by the first method, whereas curves 5 and 6 were obtained by the second method.

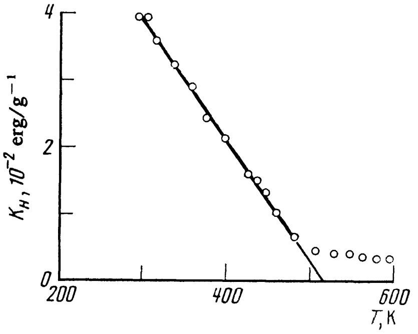

FIG. 2. Temperature dependence of the induced anisotropy $Li_3Fe_2(PO_4)_3$.

the L (ϑ) curves for any field (curve 3 in Fig. 1 was obtained in $H = 10$ kOe). We concluded from curve 3 that the magnetic-field-induced anisotropy was unidirectional. The reduction in the torque L obtained for $\varphi = \pi/2$ (curve 5) on increase in the magnetic field (inset in Fig. 1) demonstrated that the torque induced by the field along ϑ_0 was partly destroyed by the field applied along $\vartheta_0 + \pi/2$. Therefore, measurements of L (H) carried out on increase in the magnetic field (curve 5) did not coincide with the L (H) curve determined on reduction in the field (curve 6). Curves 5 and 6 (measured for $\varphi = \pi/2$) represented the field dependences of the induced anisotropy amplitude K_H measured by the second method in rising and falling fields, respectively, whereas curve 4 was obtained by the first method. In fields below 10 kOe, curves 4 and 5 were identical, whereas in $H > 10$ kOe the induced anisotropy amplitude recorded by the first method rose on increase in the field (the anisotropy amplitudes induced along different directions were additive), whereas the second method caused a reduction in the anisotropy (as pointed above, the anisotropy was destroyed).

Figure 2 shows the temperature dependence of the anisotropy K_H induced by a field of 10 kOe. It is clear from this figure that K_H fell on increase in temperature. The temperature found by extrapolation of the linear part of $K_H(T)$ to the abscissa coincided with the point of the superionic phase transition. The fall of the magnetic anisotropy toward the superionic transition temperature could be explained naturally by destruction of the internal crystal field. Consequently, disordering ("melting") of the lithium sublattice of $Li_3Fe_2(PO_4)_3$ on increase in temperature did not occur abruptly, as postulated in Ref. 2, but continuously.

The Mössbauer spectra of $Li_3Fe_2(PO_4)_3$ (obtained using a source in the form of ^{57}Co in Cr) were recorded in the temperature range 300–600 K (Fig. 3) and consisted of a quadrupole doublet typical of trivalent iron in the paramagnetic state. In the temperature interval 430–520 K the quadrupole splitting decreased by a factor of two and this again indicated a gradual modification of the crystal structure of the sample in this temperature range.

Figure 4 shows the temperature dependence of the magnetization σ in a field of 3 kOe. Below 20 K the $Li_3Fe_2(PO_4)_3$ crystal became a weak ferromagnet (magnetization curves below this temperature were described by the formula $\sigma = \sigma_0 + \chi H$) with a spontaneous magnetization $\sigma_0 = 1$

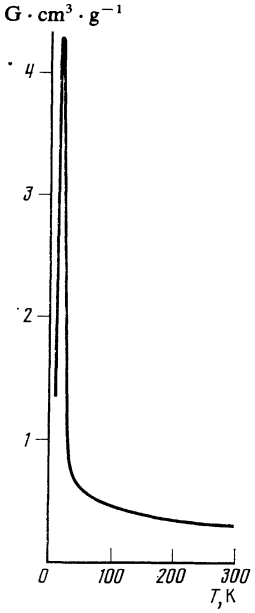

FIG. 3. Mössbauer spectra and temperature dependence of the quadrupole splitting ΔE for $Li_3Fe_2(PO_4)_3$: a) 428 K; b) 485 K; c) 520 K.

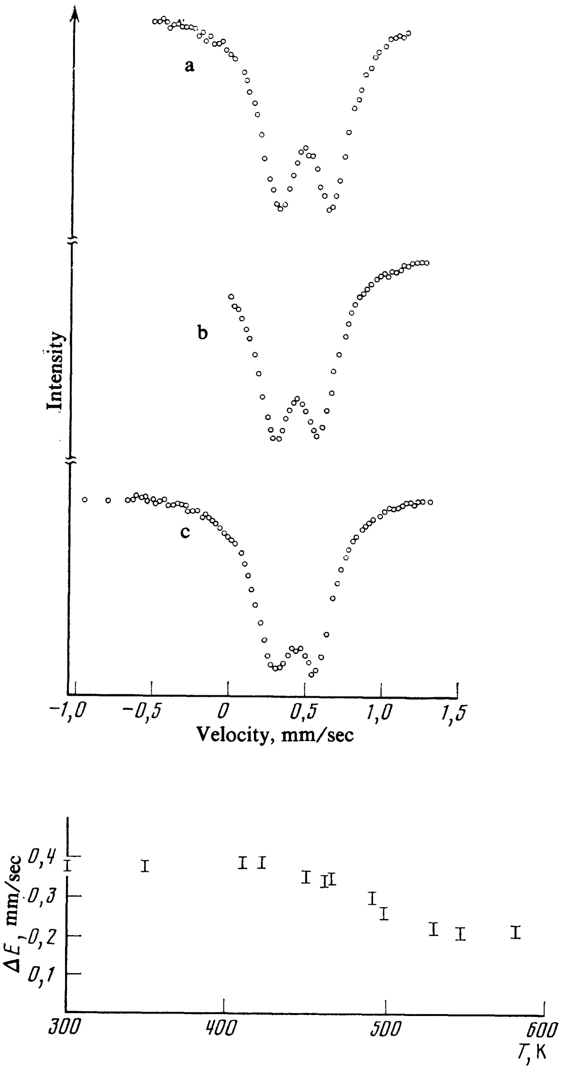

FIG. 4. Temperature dependence of the magnetization of $Li_3Fe_2(PO_4)_3$ in a magnetic field of $H = 3$ kOe.

$G \cdot cm^{-3} \cdot g^{-1}$. Above 20 K there was a long magnetization "tail."

We shall now consider the nature of magnetic properties of a $Li_3Fe_2(PO_4)_3$ crystal above 20 K. Two conclusions can be drawn from the experiments. The first is that $Li_3Fe_2(PO_4)_3$ crystals are in the spin glass state in this temperature range. This is supported by the existence of a fairly strong field-induced unidirectional magnetic anisotropy destroyed only by heating above a certain temperature. The absence of the coupling between the magnetic anisotropy and crystallographic axes may be due to damage to the crystal (disordering of the lithium sublattice[2]) which occurs continuously as temperature is increased. In a classical spin glass such as a copper-manganese alloy, Ivata *et al.*[3] observed precisely the same unidirectional anisotropy as in our case.

The competition between the exchange interactions in a spin glass means that the magnetic moments have an arbitrary orientation which is frozen below a certain temperature. Therefore, there is no overall magnetization. After application of a magnetic field and its switching off a residual magnetization M_R appears because of potential barriers that pin a certain number of magnetic moments in the field direction.[4] The unidirectional anisotropy K_H observed in our experiments can be explained by a residual magnetization: $K_H = M_R H$; M_R for a spin glass varies with time. The relaxation times are different for different spin glasses and can amount to many days. We attempted to find the change in K_H [and, consequently, in M_R if $Li_3Fe_2(PO_4)_3$ has a spin glass state], but the torque (and M_R) did not change in six hours.

The second conclusion which can be drawn is associated with the existence of the magnetization tail above 20 K (Fig. 4) extending to several hundreds of degrees Kelvin above the phase transition point. The anisotropy which is then observed is associated with the short-range order.

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