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Magnetic Moment of Lanthanum Magnetoplumbite Ferrite

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The composition $\mathrm{La^{3+}Fe^{2+}Fe_{11}^{3+}O_{19}}$ was prepared by sintering the oxides, and its magnetic moment was measured from liquid air temperature to the Curie point. At the lowest temperature a value of 17.5 Bohr magnetons per formula weight was obtained, as compared with 19 Bohr magnetons of $\mathrm{BaFe_{12}^{3+}O_{19}}$. The difference is qualitatively understood if the $\mathrm{Fe^{2+}}$ ion is a nearest neighbor to the $\mathrm{La^{3+}}$ in the crystal, i.e., in the $[12K]$ site, thus decreasing the total magnetic moment. The Curie temperature is 695°K, compared to 725°K of $\mathrm{BaFe_{12}^{3+}O_{19}}$. The lower Curie point can again be qualitatively explained by less exchange interaction with the divalent iron of $\mathrm{LaFe^{2+}Fe_{11}^{3+}O_{19}}$, or possibly by the change in unit cell dimension which modifies the short-range exchange interaction between the iron ions.

THE magnetoplumbite ferrite $M^{2+}\mathrm{Fe_{12}^{3+}O_{19}}$ was investigated[1] with M standing for $\mathrm{Ba^{2+}}$, $\mathrm{Sr^{2+}}$, or $\mathrm{Pb^{2+}}$. Deschamps and Bertaut[2] substituted fully or partially the Ba by lanthanum, which they assumed was divalent, but did not give any magnetic data. Roth and Hasko[3] have prepared the La-Al magnetoplumbite, $\mathrm{La\text{-}Al_{11}O_{18}}$, but not the iron variety. Recently, Morruzi and Shafer[4] studied the phase equilibria in air for the La-Fe-O system, but again they did not give the magnetic moment.

We have prepared the magnetoplumbite $\mathrm{La^{3+}Fe^{2+}Fe_{11}^{3+}O_{19}}$ by direct mixing of the appropriate oxides and firing at 1390°C for 48 hr followed by a rapid air quenching to room temperature. The $\mathrm{La_2O_3}$ was prefired at 1000°C for one hour in order to decompose possible hydrate or carbonate. The samples thus prepared had some $\mathrm{Fe_3O_4}$ impurities. These were dissolved in 10% $\mathrm{H_2SO_4}$, which was found to dissolve the magnetite much more than the magnetoplumbite. The reaction took place in a magnetic separator shown in Fig. 1, and was carried on until x-ray powder diffraction showed only the magnetoplumbite phase.

For chemical analysis, samples were dissolved in concentrated HCl. The $\mathrm{La^{3+}}$ was separated and quantitatively determined as oxalate. The iron chloride was passed through a silver reductor, thus enabling a volumetric determination of the total contents with $\mathrm{K_2Cr_2O_7}$. To determine the amount of $\mathrm{Fe^{2+}}$, a sample was dissolved in concentrated HCl under a strong flow of $\mathrm{CO_2}$, followed by a rapid titration with $\mathrm{K_2Cr_2O_7}$ in a $\mathrm{CO_2}$ atmosphere. The results were a ratio of 1:11 of divalent to trivalent iron, thus giving the formula $\mathrm{LaFe^{2+}Fe_{11}^{3+}O_{19}}$.

The magnetic moment was measured by the ponderometric technique[5] in a magnetic field of up to about 12 000 oersteds. The samples were finely divided powders which were mixed with a binder and allowed to set in a magnetic field. The results for the magnetic moment of the lanthanum ferrite are plotted in Fig. 2 as a function of temperature. The same figure shows also the data for a similarly prepared and measured barium ferrite. The lower limit of our temperature range is too high for extrapolating to absolute zero, but it seems rather conclusive that the La ferrite, which has a somewhat lower magnetic moment than the Ba ferrite, would extrapolate to about 19 Bohr magnetons per formula weight, or only slightly more. Pauthenet[6] obtained roughly 19.5 Bohr magnetons at liquid helium. Results somewhat higher than ours were obtained by Morruzi[7] at room temperature.

The results can be explained by assuming the $\mathrm{Fe^{2+}}$ to be one of the nearest neighbours of the $\mathrm{La^{3+}}$ in the

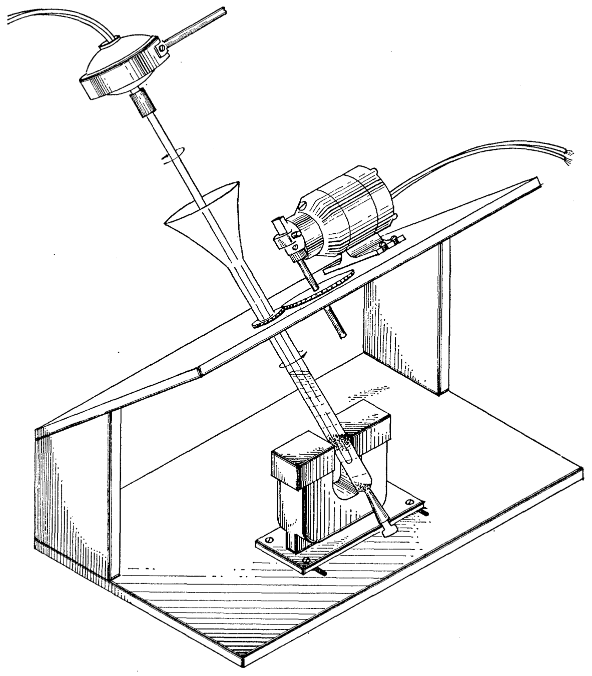

Fig. 1. Magnetic separator in a liquid medium of fine-divided powders. A cylindrical tube is rotated in a magnetic field by a motor. A glass rod is rotated in an opposite direction by a second motor.

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[2] A. Deschamps and F. Bertaut, Compt. rend. **244**, 3069 (1954).

[3] R. S. Roth and S. Hasko, J. Am. Ceram. Soc. **41**, 165 (1958).

[4] V. L. Morruzi and M. W. Shafer, J. Am. Ceram. Soc. **43**, 367 (1960).

[5] G. W. Rathenau and J. L. Snoek, Philips Research Repts. **1**, 239 (1948).

[6] R. Pauthenet (private communication).

[7] V. L. Morruzi (private communication).

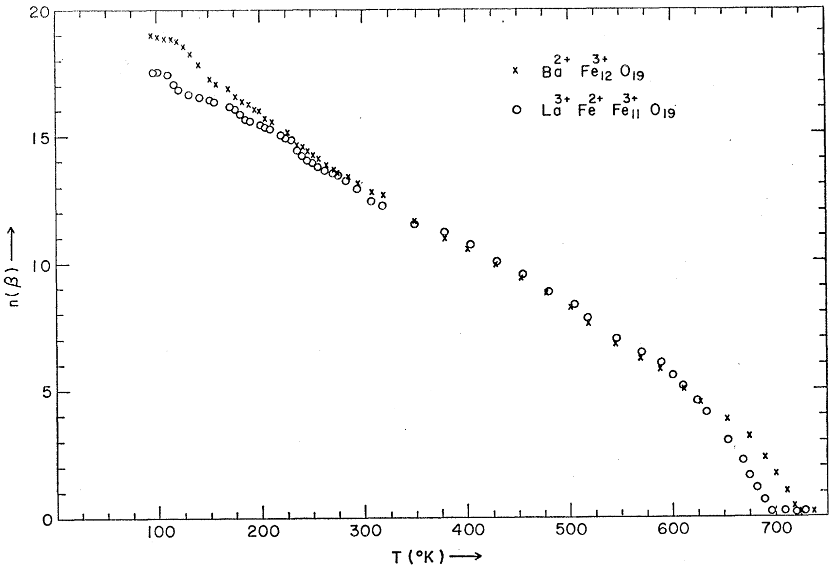

FIG. 2. The saturation magnetization $n(\beta)$ in Bohr magnetons of Ba and La ferrites as a function of the absolute temperature T.

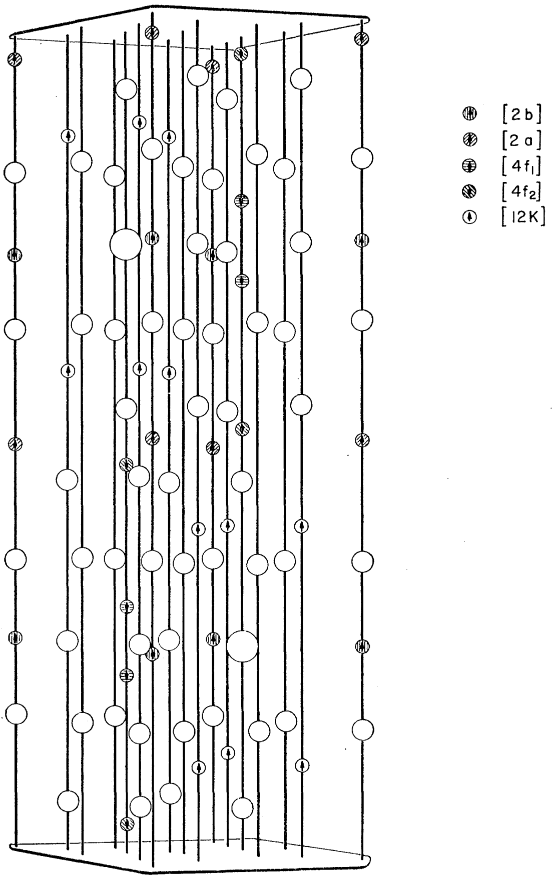

FIG. 3. The structure of magnetoplumbite crystal. The large spheres are the Ba^{2+} ions which may also be replaced by La^{3+} ions. The smaller spheres are irons whose sites are described in the figure. The spheres without any arrows are the oxygen ions.

crystals, or rather that the extra electron is shared by all of the 6 irons in the [12*K*] octahedral site. A divalent iron at this site should *reduce* the magnetic moment by one Bohr magneton as compared to a trivalent iron ion, thus yielding 19 μ_B instead of 20 μ_B of the Ba ferrite. This argument is demonstrated in Fig. 3, which shows the atoms arrangement in the magnetoplumbite,[8,9] with the [12*K*] nearest neighbors to the Ba or La ion.

As a further check on the model, two samples of a mixed composition $La_xBa_{1-x}Fe_{12}O_{19}$ (with $x=0.2$ and 0.5) were prepared by firing $BaCO_3$, La_2O_3, and Fe_2O_3 in the appropriate ratios at 1350°C for 24 hr.

After washing with 10% H_2SO_4 until pure magnetoplumbite phase was seen by x rays, the value of x was checked by chemical analysis. The magnetic moment was found to be intermediate between Ba and La ferrites, i.e., about 18 Bohr magnetons for both samples, at liquid air temperature.

The Curie temperature of $La^{3+}Fe^{2+}Fe_{11}{}^{3+}O_{19}$ was found to be 695°K, as compared with 725°K of the Ba ferrite. This can be expected, because of the smaller exchange interaction[10] with the divalent iron. The Curie points of the $x=0.2$ and $x=0.5$ samples were about 715°K and 710°K as determined by the Differential Thermal Analysis technique.[11]

Kittel has suggested that most of the lowering in the Curie point in the La plumbite might be explained by the smaller unit cell dimensions[2,4] compared with that of Ba ferrite. Here a change of 1.2% in the unit cell

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[9] F. Bertaut, A. Deschamps, and R. Pauthenet, Compt. rend. **246**, 2407 (1958).

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dimension causes a change of 4% in the Curie point and this is a reasonable change in view of the experiments on change of the Curie point by hydrostatic pressure.[12]

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Effective X-Ray and Calorimetric Debye Temperature for Copper

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The Debye-Waller factor for copper was determined from x-ray intensity measurements on a single crystal over the temperature range 4.2°K–500°K. From a machine calculation of the vibrational spectrum of copper the values of the specific heat and Debye-Waller factor were obtained and compared with those found by experiment. The agreement indicates that for copper the central force model with nearest- and second-neighbor interactions is adequate for the interpretation of effects depending on simple averages over the frequency spectrum.

INTRODUCTION

EXPERIMENTAL data on the Debye-Waller factor for x-ray reflections have hitherto been interpreted in terms of the theory for an ideal Debye solid. The general theory for an elastic solid has been available for many years,[1] and has been applied to an analysis of the diffuse scattering[2]; there has been no corresponding analysis of the elastic scattering. Attempts to correlate calorimetric data with x-ray results on the basis of the simple Debye theory have been somewhat inconclusive.

To remedy this situation, we chose copper as a solid whose elastic properties have been extensively investigated down to 4°K, and for which accurate calorimetric data are available over a wide temperature range. We made corresponding x-ray intensity measurements over the temperature range 4.2°–500°K. We also carried out a machine calculation of the vibrational spectrum of copper, and compared the predicted values of specific heat and Debye-Waller factor with those obtained experimentally.

DETAILS

The x-ray measurements were performed on a single crystal of copper grown from the melt by the usual Bridgman technique. A slice was cut so as to expose a (100) face, and was polished electrolytically to remove the cold-worked layer and annealed in vacuum. The crystal was then mounted in the cryostat shown in Fig. 1. The cryostat is constructed of thin-wall stainless steel tubing, with over-all dimensions approximately 15 in. in height and $4\frac{1}{2}$ in. in diameter. The liquid coolant is held in the 250-cc chamber L, surrounded by, successively, a vacuum chamber V, a secondary cooling well K, and again the vacuum chamber V. The specimen chamber S is enclosed by a copper radiation shield with an aluminum foil window. A 10-mil thick beryllium strip soldered onto a semicircumferential slot in the outer wall of the cryostat permits x rays to enter and leave the specimen chamber. Under a good vacuum (10^{-6} mm) the cryostat will hold liquid helium for almost 24 hours.

In order to align the crystal for maximum reflected intensity two degrees of freedom are needed in the specimen mount, which is shown in detail in Fig. 2. The single crystal is clamped on the flat plate M, which is free to rotate in its own plane in a bearing in the cradle C. Similarly, the cradle C is held on bearings in the base mounts B attached to the liquid chamber L. All parts, B, C, and M, are of copper. A screw T pushes against the cradle C so as to tilt the crystal out of the plane of the axis of the cryostat, and a screw R pushes on the mount M to produce a rotation of the crystal in its own plane. For x-ray measurements, the cryostat was mounted on a Berthold spectrometer equipped with a NaI(Tl) scintillation counter. To obtain high-index reflections, we used Mo $K\alpha$ radiation, crystal-monochromated to minimize background. By the method described in a previous paper[3] we measured the integrated intensities of the (600), (800), and (1000) reflections at selected temperatures between 4.2° and 500°K. To correct for the diffuse scattering component of the measured intensity, the diffuse intensity adjacent to the Bragg peaks was extrapolated to the peak region, and this value was subtracted from the observed main

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[1] R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, London, 1954), Chap. V.

[2] See, e.g., E. H. Jacobsen, Phys. Rev. **97**, 851 (1954).

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