observed spectrum, we have attempted to investigate the nature and extent of the modification which must be attributed to the inner level if the observations are to be essentially in accord with the computed band shape (to the extent that such a modification may be treated mathematically as a folding operation). In this connection the integral in Eq. (6) was evaluated by taking $\chi(E)$ proportional to $E^{\frac{1}{2}}$ and by regarding $S(E,E')$ to be either Lorentizian or Gaussian in form. The process of matching the observed distribution $I(E)$ was subject to the choice of two parameters; namely the width adopted in characterizing the spectral window and the value of E taken to designate the high-energy limit of the domain over which the $E^{\frac{1}{2}}$ behavior was assumed to hold.

The results of these integrations indicate that folding with the Lorentzian distribution will not reproduce the experimental curve for the emission band. The long "tails" characteristic of this distribution are emphasized in the integrated result and do not have their counterpart in the experimental shape. Much better agreement is obtained when the modifying function is taken as Gaussian. For a Gaussian distribution with a half-width of 0.35 ev and for an energy range of 2.8 ev for the function $\chi(E)\sim E^{\frac{1}{2}}$, it is possible to reproduce quite well the observed band shape.

In addition to the band shown in Fig. 1, examination of the spectrograms reveals a second band, less intense than the band at 227 A, with a high-energy edge at 148.4 A (a displacement toward higher energies of 29 ev from the band edge of Fig. 1). This band has a rather broad maximum centered at 82.83 ev, a drop in intensity to one-half of peak value on the high-energy side at 83.54 ev, a full width at half-maximum of 1.90 ev, and a full band spread of 5.0 ev. In appearance it resembles closely the lithium K band portrayed in Fig. 1. It does not seem possible to identify this second band with the characteristic spectrum of any impurity likely to be present at the target. The band in question has been observed on all plates exposed to the lithium radiation, and in each case the peak intensity of the weaker band at 148.8 A bears the same ratio (1/10) to the peak intensity of the lithium band at 227 A. This second band has tentatively been identified as a lithium K satellite and its origin is attributed to double excitation of the K shell.

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Loss of Exchange Coupling in the Surface Layers of Ferromagnetic Particles

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Experiments with spherical iron particles 28 A to 265 A in diameter demonstrate that the proposed nonferromagnetic surface layer on an iron particle must be less than 1 A thick. This conclusion is based upon a comparison of the ferromagnetic iron indicated by magnetic saturation, and the total amount of iron as determined by chemical analysis.

IT has been proposed[1] that the saturation magnetization of thin layers at temperatures above absolute zero should decrease with thickness because of a decrease in Curie temperature caused by a weakened exchange coupling. For films or particles in the angstrom size range the atomic layers involved would account for a large fraction of the volume thus reducing the saturation induction greatly. Such behavior has been reported, for example, in the case of thin nickel films.[2]

The magnetic properties of ultrasmall particles are of interest because of their excellent permanent magnet characteristics. Magnets composed of elongated fine particles of iron and iron-cobalt have been made with energies up to 5×10^6 gauss-oersteds.[3,4] However, the theoretical upper limit of energy for magnets composed of ideally elongated particles of iron is 40×10^6 gauss-oersteds. The difference between experiment and theory has been accounted for mainly by nonideal particle shape, particle misalignment, particle size and shape distribution, and imperfect packing of the particles.[4,5] The magnitude of the loss in induction due to the loss in exchange coupling at the surface is an additional factor to be considered.

Becker[6] has shown that cobalt precipitated in solid copper has a nonmagnetic layer less than 1 A in thickness at room temperature. An analysis of measurements

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made on spherical iron particles dispersed in liquid mercury reported in this paper substantiates Becker's results. Thus, the loss of ex hange coupling at the surface of fine particles need not be considered in theoretical calculations of permanent magnet properties.

EXPERIMENTAL

Spherical particles were made by electrodepositing iron into mercury from an aqueous ferrous chloride solution. The particles prepared by this method had a median diameter of about 25 A. The dispersions of iron in mercury were then heated to a particular temperature to produce colloidal iron particles of a definite average diameter. The median particle size was determined from coercive force measurements made at liquid nitrogen temperatures, making use of the previously established correlation between coercive force and particle size.[7] Test bars were then pressed from the mercury phase; finely-divided lead was added to prevent breakage during testing. The measurements described below were made as soon as the test bars were pressed, although no weight change, to $\pm 0.05\%$, due to oxidation was noticeable even after several hours.

The saturation induction of the sample at 25°C was obtained from permeameter measurements made in magnetizing fields up to 10 000 gauss by extrapolating to infinite field. For the samples containing particles in the "superparamagnetic" size range, i.e., below about 100 A, the high-field approximation of the Langevin function was used as described by Bean and Jacobs.[8] For the larger particles a $1/H$ extrapolation was used. From these saturation inducti ns and the densities as determined from size and weight measurements, the fraction of magnetic iron in the sample by weight was calculated, i.e.,

$$f_{\text{mag}}=I_0 d_{\text{Fe}}/I_s d_0,$$

where $d_{\text{Fe}}=7.86$ g/cc, $I_s=1720$ gauss, and d_0 and I_0 are the corresponding density and intrinsic saturation induction of the sample. The ratio of this magnetic iron in the sample to the total iron as obtained by direct chemical analysis thus gave the fraction of the total iron in the particles which was magnetic. The amount of iron dissolved in the mercury was negligible.

RESULTS AND DISCUSSION

The results of the measurements are shown in Fig. 1 as a function of particle size compared to calculated curves assuming various thicknesses of nonmagnetic iron at the surface of each particle. This comparison indicates that any nonmagnetic iron present corresponds to a surface layer less than 1 A thick.

A possible error arises in the use of the high-field approximation of the classical Langevin function[8] to extrapolate the induction of samples to infinite field.

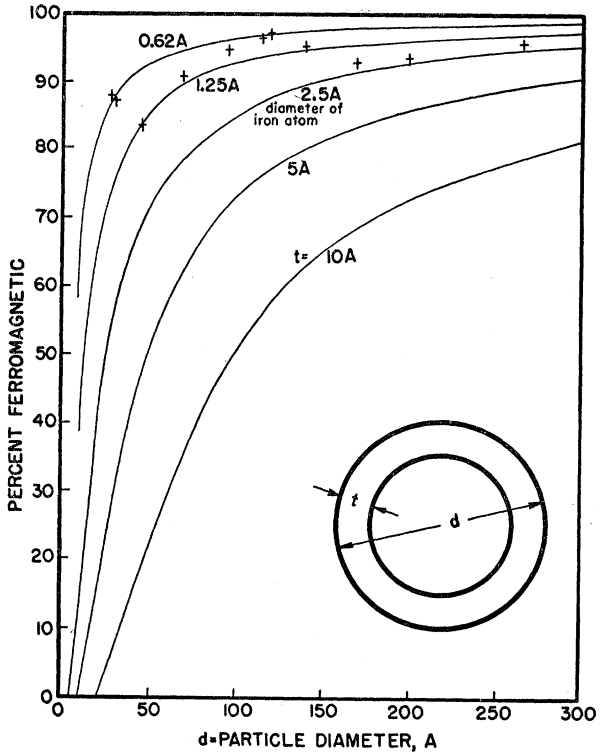

FIG. 1. Reduction in saturation magnetization of spherical particles resulting from "nonmagnetic" surface atoms contained in a spherical shell of thickness t. Experimental results are shown by the crosses.

In Fig. 2 is shown the plot of the data for particle sizes below 115 A fitted to the Langevin function whose linear approximation at high fields is given by

$$\frac{I}{I_0}=1-\frac{kT}{VHI_s}=1-\frac{kT}{\mu H},$$

where I_0, the saturation induction of the magnet, is adjusted to give the best fit to a smooth curve. The median particle sizes of the samples are shown on the curve. The samples containing median particle sizes of 96 A or greater do not fall on the curve as expected since they are too large to be superparamagnetic. I_0 was obtained more readily in these cases from a $1/H$ extrapolation as previously described. Particles in the superparamagnetic size range, which includes the four samples with median particle diameters of 70 A and less, do appear to follow the Langevin function initially, but deviations from linearity occur at $I/I_0 \sim 0.9$ in the experimental curve rather than at ~ 0.7. This may be accounted for, in part, by the particle size distribution present. The particle diameter distribution for these colloidal iron dispersions has been determined at one diameter, 150 A, as previously reported.[7] The volume distribution function calculated from these data is considerably skewed, with the peak

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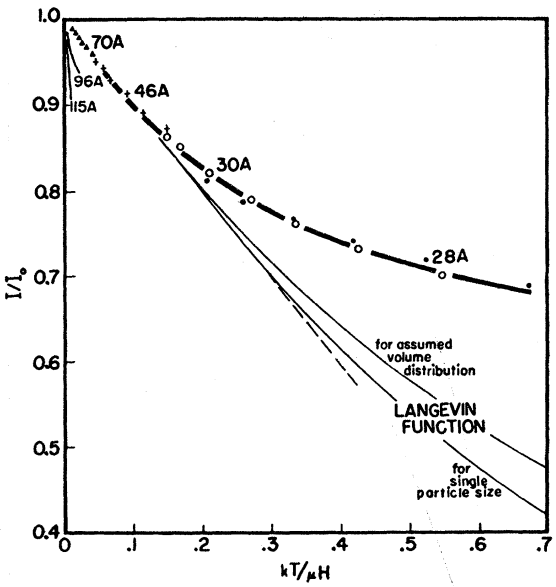

FIG. 2. High-field magnetization of spherical iron particles in mercury at 25°C. The symbols ▲, +, ○, and ● correspond to median particle sizes of 70 A, 46 A, 30 A, and 28 A, respectively.

of the distribution falling below the mean particle volume. The numerical integration of the Langevin function, $L(x)=L(VI_sH/kT)$, over this volume distribution, i.e., $\int L(VI_sH/kT)dV$, results in the curve labeled "for assumed volume distribution" in Fig. 2. This calculated curve approaches the experimental curve more closely than does the curve for the single particle size; it deviates from linearity (the dashed line in Fig. 2) at a value of $I/I_0 \sim 0.8$. It is expected that the volume disribution of these very small particles should be considerably broader than the 150 A particles whose distribution was determined. This would further reduce the difference between the calculated curve and the experimental curve.

Another error affecting the agreement between the experimental and theoretical curves is due to the particle size estimates made from coercive force measurements. Kinetic studies[7] of the growth of iron particles in mercury indicate that the correlation between coercive force and particle diameter yields diameters which are somewhat high in the size range below 100 A. Using a smaller median particle diameter would increase the extrapolated saturation induction and move the experimental curve closer to the calculated curve, reducing even further the estimated thickness of the nonmagnetic layer.

Calculations were also made to obtain the saturation induction of the superparamagnetic particles without using the Langevin function, using instead the $1/H$ extrapolation. The saturation induction obtained in this way for the smallest particle size was 10% less than that obtained with the Langevin function. For the larger particle sizes the differences became smaller. This simplified approach still corresponds to only a 1 A nonmagnetic layer.

The constancy of the data in the particle size range above 100 A suggests that there may be a consistent discrepancy between the chemical and magnetic analysis of about 5%. This error cannot be accounted for, but correcting this error would also reduce the calculated thickness of the nonmagnetic layer.

Mayer and Vogt[9] reported a loss in saturation magnetization at room temperature of up to 50% for iron particles in mercury in the size range studied in this work. As shown by Bean and Jacobs,[8] this was due to incorrect extrapolation of the magnetization of the samples to infinite field. The results in this work substantiate the conclusions of Bean and Jacobs, but are in sharp contrast to the results of work on thin films.[1,2]

CONCLUSIONS

These results and analyses show that a 1 A nonmagnetic layer may be present on the surface of colloidal iron particles dispersed in liquid mercury. The analyses of possible errors indicate that this thickness may be considerably less. Thus, there will be a negligible decrease in saturation induction due to the loss of exchange coupling at the surface of iron particles greater than 100 A in diameter.

It appears that the approach to saturation of the particles in the superparamagnetic size range must be described by the Langevin function. In addition, the size distribution of the particles in the sample should be considered. The $1/H$ extrapolation gives values which are low.

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