

explaining the shortness of the lifetime observed in insulators and provide another means by which triplet positronium may be rapidly converted to singlet positronium. The length of the covalent bond when compared with the lattice parameters could also provide criteria determining whether or not such compounds could be formed.

Clearly a great deal of work must be done to be sure that the effects reported here are reproduced in other superconductors. The dependence of the observed

lifetime change on the crystal structure of the superconductor could, for example, be checked. There are many other such problems immediately presented. Experiments are being continued here along these and other lines relating to positron life times in solids.

The authors are deeply indebted to Professor M. Dresden for many valuable discussions of the problem. They are also grateful to Dr. G. G. Wiseman and Mr. J. D. Wackerle for the considerable time spent in maintaining a supply of liquid helium.

Critical Field Phenomena in an Isotropic Paramagnetic Crystal

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(Received July 9, 1954)

Measurements have been made of the variation of magnetic moment with applied field, at constant entropy, for a spherically-ground single crystal of chromic methylammonium alum. Steady fields up to 500 oersteds were applied along a cubic axis of the crystal and the differential susceptibility measured ballistically by reversing a field of 1.7 oersteds in the primary of a mutual inductance surrounding the specimen. The total magnetic moment was obtained by integration. At entropies below that of the "Curie point" the differential susceptibility showed a pronounced maximum in a field of about one hundred oersteds. This behavior is compared with that observed in earlier measurements on the same specimen in transverse fields. The magnetic moment at constant external magnetic field H , plotted as a function of entropy, shows a maximum for small values of H . The locus of these maxima is evidently a transition curve separating regions of paramagnetic and antiferromagnetic behavior.

1. INTRODUCTION

SINCE the earliest investigations of the behavior of paramagnetic salts at very low temperatures, reached by means of the technique of adiabatic demagnetization, considerable interest has been centered on the phenomena associated with the appearance of a susceptibility maximum.¹ These include hysteresis and remanence observed in dc measurements, a complex ac susceptibility (ac losses), and a negative magnetocaloric effect—evidence of cooperative effects which have been generally ascribed to the onset of antiferromagnetic behavior.²

More recently Garrett³ has reported measurements made on an anisotropic paramagnetic crystal, cobalt ammonium sulfate, in which an interesting effect was observed below the Curie point for fields applied along the K_1 (strong magnetic) axis—namely, that the differential susceptibility at constant entropy S increased with increasing magnitude of the polarizing field, reaching a fairly sharp maximum in fields of a few hundred oersteds. By measuring absolute temperatures in zero field, and by calculating increments of temperature as a function of field along an isentropic,

using the thermodynamic formula

$$(\partial T / \partial H)_S = -(\partial M / \partial S)_H \quad (1)$$

(where M is the magnetic moment of the specimen), Garrett was able to plot on a $T-H$ diagram a lattice of isentropic and isomomental curves. The locus of the minima of both sets of curves described a phase boundary which was identified as delineating the transition from antiferromagnetic to paramagnetic behavior, since the features of the diagram showed striking similarity to the predictions of a theory due to Sauer and Temperley⁴ postulating antiparallel ordering at very low temperatures through dipole-dipole interaction.

In a recent investigation of the low-temperature magnetic properties of chromic methylammonium alum, a salt which is magnetically isotropic in the region of 1°K, Hudson and McLane⁵ obtained indications of similar behavior of the susceptibility below the Curie point. The measurements were made with a transverse polarizing field, the measured susceptibility being assumed to be equal to M/H , as is true for an isotropic material. The indications were, however, that the salt was definitely not isotropic, at least in fields greater

¹ Kurti, Laine, Rollin, and Simon, *Compt. rend.* **202**, 1576 (1936).

² N. Kurti, *J. phys. et radium* **12**, 281 (1951).

³ C. G. B. Garrett, *Proc. Roy. Soc. (London)* **A206**, 242 (1951).

⁴ J. A. Sauer and H. N. V. Temperley, *Proc. Roy. Soc. (London)* **A176**, 203 (1940).

⁵ R. P. Hudson and C. K. McLane, *Phys. Rev.* **95**, 932 (1954).

than 100 oersteds, and it was thought worth while to repeat these measurements with the same crystal in longitudinal fields, measuring a differential susceptibility and obtaining the magnetic moment M by integration. The present paper describes these latter experiments.

2. APPARATUS AND PROCEDURE

The method of mounting the crystal within the cryostat and the details of the measuring equipment have been described in an earlier publication⁵ and need not be repeated here. The transverse field measurements had been made with a small ac measuring field of 210 cps frequency. To avoid the strong coupling effects between the coaxial solenoid and "measuring coil," ballistic determinations of the differential susceptibility were made. It is not unlikely that by making ac measurements (with reduced coupling by suitable design of the measuring coil)⁶ somewhat different values of the susceptibility would be obtained.

After adiabatic demagnetization, the cryostat was swung out of the magnet into a framework which supported earth's field compensating coils and a small solenoid capable of producing fields up to 500 oersteds. Susceptibility measurements were commenced within thirty seconds, the throw of a ballistic galvanometer being observed for a reversal of a 1.72 oersteds measuring field in the primary coil of the cryostat mutual inductance. The sensitivity of measurement was increased by the familiar procedure of compensating by means of an external mutual inductance the greater part of that in the cryostat and observing the effect of the remainder on the galvanometer, which could then be used at full sensitivity. [The response was

found by calibration to be 0.568-mm deflection per microhenry. The uncompensated part of the mutual inductance was generally of the order of 100 microhenries; galvanometer deflections could be read with an accuracy better than 0.2 mm. The total mutual inductance to be measured varied, in general, between 400 and 700 microhenries, but fell as low as 30 microhenries for measurements of the differential susceptibility in fields of the order of 500 oersteds. The period of the galvanometer was 5.6 seconds.] The polarizing field was increased in steps, three or four susceptibility determinations being made for each value of the field. By plotting all the readings as a function of time and extrapolating to time zero, values were obtained for the differential susceptibility as a function of polarizing field for the particular entropy of that demagnetization.

The stray heat leak to the specimen, estimated to be about 50 ergs per minute, proved to be sufficiently small to ensure a small probable error in the aforementioned extrapolation despite the necessity of pursuing the measurements for some twelve minutes after demagnetization.

3. RESULTS

As a check on the quality of the specimen, which had been stored in a closed vessel at 0°C for seven months, the $S-T^*$ relation was measured over the range 0.077 to 0.476 degree T^* . Exact agreement was obtained with previously published data (reference 5, Single Crystal II). In the immediate neighborhood of the Curie point, however, the zero-field susceptibility appeared to be some five percent too small to fit in with the series of ballistic measurements (using rather higher measuring fields) made when this crystal was placed in the cryostat for the first time. The values were very close, in fact, to those obtained for another specimen (Single Crystal I) with the same measuring field. As noted in reference 5, this degree of nonreproducibility of χ in the region of χ_{\max} appears to be associated with differences in the rates of precooling.

The variations of isentropic differential susceptibility $(\partial M/\partial H)_S$ with field H for various entropies is shown in Fig. 1.⁷ For entropy greater than that of the Curie point (i.e., S/R greater than 0.53), normal saturation behavior is observed and $(\partial M/\partial H)_S$ decreases continuously as H is increased. Just below the Curie point, however, the behavior is strikingly different; up to about 20 oersteds the susceptibility decreases slightly with increasing field; beyond this point it increases rapidly and then goes through a maximum. As the entropy is progressively lowered, the initial dip in $(\partial M/\partial H)_S$ tends to disappear while the subsequent maximum becomes more pronounced and a side peak develops.

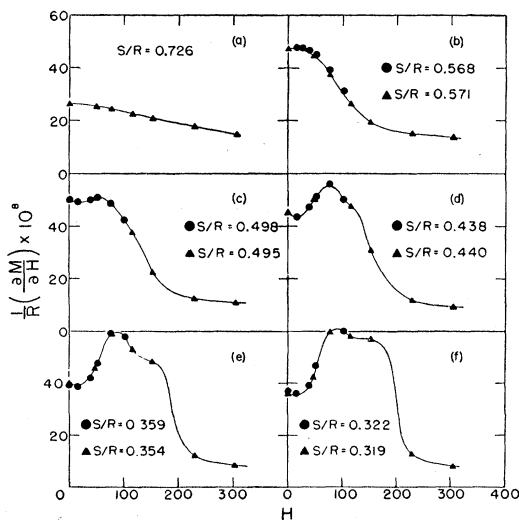


FIG. 1. Isentropic differential susceptibility as a function of external field at various entropies, for chromic methylammonium alum.

⁶ Casimir, Bijl, and du Pré, *Physica* 8, 449 (1941).

⁷ In this paper the not uncommon practice is adopted of dividing magnetic and caloric quantities, scaled to 1 gram ion of salt, by the gas constant R . It is however, frequently convenient to omit the " R " when employing a symbol as an abbreviation for the name of a quantity in the text.

By integrating the curves of Fig. 1 one may obtain the magnetic moment as a function of field at the corresponding entropies and the $M-H$ curves are shown in Fig. 2. In some cases, measurements of M at almost identical entropies had been obtained in the earlier transverse field measurements (but using an ac measuring field) and these are represented in Fig. 2 by the broken lines. Since these latter curves were derived on the assumption of isotropic behavior, that is, by assuming that the apparent susceptibility was equal to M/H , any marked differences in a pair of curves at a given entropy should be evidence of a breakdown of the relation due to *anisotropic* behavior. It would seem, therefore, from our results that the salt is markedly anisotropic at low entropies in fields greater than about

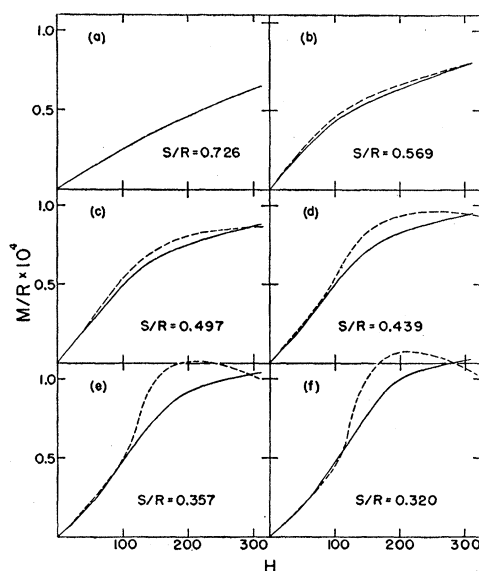


FIG. 2. Magnetic moment as a function of external field at various entropies, obtained by integration of curves of Fig. 1. Full lines, measurements in longitudinal field; broken lines, transverse-field results at corresponding entropies taken from reference 5.

100 oersteds. As the Curie point is approached, anisotropy is evidenced in progressively smaller fields, and the measurements suggest that a detectable anisotropy exists for all values of H at entropies close to and on either side of the Curie point.

The results may be presented in yet a third manner, namely, a plot of magnetic moment M versus entropy S for constant values of the static field H . This is given in Fig. 3. For fields up to 120 oersteds, the magnetic moment is seen to go through a maximum. Within the area bounded by the dashed curve, which is the locus of the magnetic moment maxima, the magneto caloric effect—or temperature change upon isentropic change of magnetic field—is negative, since $(\partial M/\partial S)_H$ is positive in this region [see Eq. (1)]. For all points outside this boundary curve, the reverse is true and

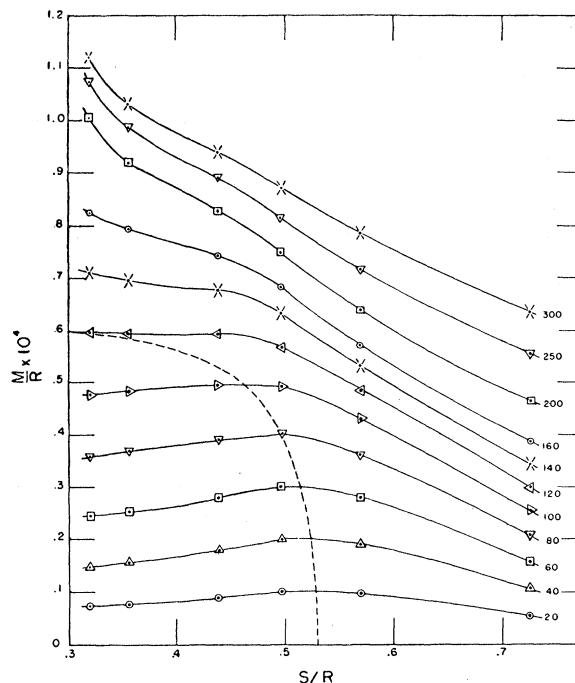


FIG. 3. Magnetic moment as a function of entropy for various values of the applied field. The broken curve is the locus of the maxima and encloses a region of antiferromagnetic behavior.

the magnetocaloric effect is positive, corresponding with normal paramagnetic behavior. At any entropy less than that of the normal Curie point a critical field H_c may be defined—namely, the value of H at that entropy as the boundary curve is crossed. It is apparent that the maxima in $(\partial M/\partial H)_S$ occur at fields slightly less than the critical values.

Since the maximum value of the critical field is so small in this salt (120 oersteds), one can readily make measurements well outside the transition curve, even at the lowest entropies. For fields greater than 120 oersteds the magnetic moment does not go through a maximum with decreasing entropy, but a tendency to do so persists up to fields of 300 oersteds (Fig. 3). This could be evidence that some type of short-range order persists after the destruction of antiferromagnetism. At the lowest entropy—highest field (upper left) portion of Fig. 3 the magnetic moment is seen to be increasing quite rapidly with decreasing entropy and it would be of considerable interest to extend these measurements to much lower entropies in order to obtain, by extrapolation, data on the variation of magnetic moment with external field at the absolute zero.

4. DISCUSSION

On comparing Figs. 2 and 3, it is seen that at entropies below that of the normal Curie point the salt is apparently isotropic—as deduced from the agreement between the present longitudinal field measurements and the earlier transverse field measurements—so long

as the external field remains less than the critical value for that entropy. As the critical field is exceeded and the paramagnetic region is entered, the salt becomes markedly anisotropic.

A negative magnetocaloric effect is readily explained for the case of antiferromagnetic ordering, since the first effect of applying a steadily increasing field will be to disrupt the symmetry of the antiparallel alignment and the order will then be *less* perfect than before.²

The symmetry of the crystalline electric field in the alums, which have a *f.c.c.* structure, is basically cubic with (even in the β -type alums) a small trigonal-component.⁸ The latter in conjunction with spin-orbit coupling, splits the ground state of the Cr^{+++} ion into two levels having $S_z = \pm\frac{1}{2}$, $\pm\frac{3}{2}$, the axis of quantization being the trigonal axis. The $\pm\frac{3}{2}$ level is lower. There are four nonequivalent ions in unit cell, each set of ions having its own trigonal axis in the direction of one of the four body diagonals of the basic cube. All the measurements were made with the external field applied along a cubic axis, so that the splitting pattern should be the same for all ions.⁹

Since the splitting δ/K is about 0.27 degree and the direct interaction is an order of magnitude smaller,^{5,10} there will be no appreciable overlap of the two sets of levels corresponding to $S_z = \pm\frac{1}{2}$ and $\pm\frac{3}{2}$, and one may use the following rough model. One retains the concept of a quantum number S_z , and as the temperature approaches the Curie point essentially all ions will have $S_z = \pm\frac{3}{2}$, i.e., they will be aligned along their trigonal axes. The ions are then behaving in a very anisotropic way, and for H less than about 200 oersteds can be described by an effective spin $\frac{1}{2}$ with a g -value given by $6 \cos\theta$, where θ is the angle between H and the trigonal axis. Thus for all ions, in the present case, the level splits according to $W = \pm\sqrt{3}\beta H$. With $H = 200$ oersted, for example, the splitting is equivalent to 0.05 degree.

On the above picture, when cooperative ordering occurs the spins will remain aligned with respect to their own trigonal axes, but there will be presumably a correlation between the directions of neighboring spins. Upon application of a small (but greater than critical) magnetic field, the ions will be largely concentrated in the lowest level $S_z = \pm\frac{3}{2}$. Hence at low entropies and in fields between 120 and (say) 200 oersteds, the spins should be polarized along their own trigonal axes, resulting in a net magnetic moment in the direction of H given by $M/R = \sqrt{3}\beta/K = 1.163 \times 10^{-4}$ degree-oersted⁻¹. [Since the process is isentropic there will be a temperature rise but one finds that up to

fields of the order of 200 oersted the effect is small and would not invalidate the above reasoning.] The actual experimental results (Fig. 2) are not inconsistent with this picture. After its steep rise in the region of the critical field the magnetic moment M increases quite slowly for further increase of H . The "knee" in the curve becomes more pronounced with decreasing entropy, and the value of M at this point appears to approach a limiting value of about the magnitude derived above.

The results presented here are similar to those obtained by Garrett³ for measurements along the K_1 axis of a single crystal of cobalt ammonium sulfate. Garrett observed a maximum in $(\partial M/\partial H)_S$ which was smooth and single, in contrast to the double-peak effect, visible in Fig. 1. These results were presented as lines of constant entropy and lines of constant moment on a $T-H$ diagram. Absolute temperature determinations have not yet been made for chromic methylammonium alum,¹⁰ but, as indicated by the thermodynamic relation in Eq. (1), an $M-S$ plot of lines of constant field is entirely equivalent. It should be pointed out that the type of behavior shown in Fig. 3 may be observed in substances which do not exhibit any striking features in the isentropic differential susceptibility. For example, the data of Kurti² for an ellipsoidal, compressed powder specimen of ferric ammonium alum showed the boundary curve feature, although $(\partial M/\partial H)_S$ was found to decrease continuously with increasing applied field over the range of entropy investigated. Again, the data obtained by Steenland¹¹ for chromic potassium alum in transverse-field measurements upon a single-crystal sphere indicate that $(\partial M/\partial S)_H$ below the Curie point is positive over a small range of external fields, whereas the susceptibility decreased with increasing field at all entropies.

The theory of Sauer and Temperley⁴ yields the following expressions for the end points of the boundary curve:—the critical temperature in zero field (normal Curie point), $T_c = 3.6\mu^2 N/k$, and the critical field at the absolute zero, $H_0 = 1.8\mu N$, where N is the number of magnetic ions per cm³, k is the Boltzmann constant, and μ is the magnetic moment of one ion. The theory, however, included the simplification of a unique direction of alignment with the external field applied parallel to that direction. In the experimental case we have the complicated situation of alignment taking place with respect to each of the four trigonal axes, while the external field is directed along a cubic axis.

For an order-of-magnitude calculation, however, one may take the component of the external field along a trigonal axis, i.e., $H/\sqrt{3}$. Substituting numerical values in the Sauer-Temperley formulas one obtains $T_c = 0.04^\circ$ and $H_0 = 100$ oersteds. The "parallel component" of the H_0 indicated by Fig. 3 (120 oersteds) is 70 oersteds, and T_c is probably about 0.02°K .^{5,10} Thus $kT_c/\mu H_0$

⁸ J. H. Van Vleck, *J. Chem. Phys.* **7**, 61 (1939); D. M. S. Bagguley and J. H. E. Griffiths, *Proc. Roy. Soc. (London)* **A204**, 188 (1950).

⁹ L. J. F. Broer, *Physica* **9**, 537 (1942).

¹⁰ W. E. Gardner and N. Kurti have recently reported [*Proc. Roy. Soc. (London)* **A223**, 542 (1954)] absolute temperature measurements with this salt in the range 0.013° – 0.396°K ; the Curie point is given as 0.02°K . These results were not available to the authors at the time of original preparation of this report.

¹¹ M. J. Steenland, Thesis, Leiden, 1952 (unpublished), p. 44.

=1.4, whereas the theory predicts the value 2 for this ratio. In view of the inadequacies of the theoretical model applied to the present case, the agreement between prediction and experience is quite good. For comparison, the results of Steenland suggest that for potassium chromic alum $H_0 \sim 15$ oersteds, and it was found by de Klerk, Steenland, and Gorter¹² that $T_c = 0.004^\circ\text{K}$. [The value of T_c obtained by Daniels and Kurti¹³ was, however, 0.011°K .]

Garrett¹⁴ has recently extended Van Vleck's exchange-interaction theory of the antiferromagnetic state and obtained the interesting result that, on this model too, a critical curve is to be expected which is not very different in form from that predicted by the Sauer-Temperley dipole-interaction theory. Garrett's theory, however, predicts unity for the ratio $kT_c/\mu H_0$. Whereas dipole interaction is present and of roughly the same order of magnitude in all low-temperature paramagnetics, exchange interaction appears only in some cases and varies greatly in magnitude in these. Kurti has pointed out¹⁵ that the discrepancy in values of δ/k , the crystalline field splitting, in chromic methylam-

monium alum derived from adiabatic demagnetization experiments,⁶ 0.269 degree, and from the most recent paramagnetic resonance measurements of Baker and Bleaney (unpublished), 0.255 degree, can be resolved if a small amount of anisotropic exchange coupling is assumed to be present in this salt. If this is the case, then exchange contributes about seven times as much as does dipole-interaction to the specific heat in the $1/T^2$ region [$b = CT^2/R = 7 \times 10^{-3}$ and 10^{-3} , respectively] and might therefore be deduced to be an important factor in bringing about the antiferromagnetic transition. On the other hand, there is no evidence (yet reported) of exchange in the potassium chromic alum. In the case of cobalt ammonium sulfate it is found⁸ that the dipole-interaction contribution to the specific heat in the $1/T^2$ region is somewhat greater than the exchange contribution: $b(\text{dipole}) = 1.9 \times 10^{-3}$ and $b(\text{exchange}) = 0.8 \times 10^{-3}$.

Thus no clear-cut picture of the relative importance of the two types of interaction in bringing about a transition emerges from the existing experimental data. Their interpretation is hampered by the fact that the much simplified theoretical models treated so far bear little relation to complicated state of affairs existing in actual crystals, where both exchange and dipole-dipole interactions may be present and where the ions themselves are magnetically anisotropic.

¹² de Klerk, Steenland, and Gorter, *Physica* **15**, 649 (1949).

¹³ J. M. Daniels and N. Kurti, *Proc. Roy. Soc. (London)* **A122**, 243 (1954).

¹⁴ C. G. B. Garrett, *J. Chem. Phys.* **19**, 1154 (1951).

¹⁵ N. Kurti (private communication).

Fluorescent Response of NaI(Tl) to Nuclear Radiations*†

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(Received July 26, 1954)

The dependence on thallium concentration of the fluorescent response of NaI(Tl) to gamma rays and charged particles has been examined for crystals containing known mole fractions of Tl in the range from 0.00006 to 0.008. Scintillations were detected with a photomultiplier tube and pulses were displayed on an oscilloscope and recorded photographically. Plots of integrated pulse height *vs* energy for alpha-particle excitation show a region of nonlinearity which decreases with increasing Tl concentration. At sufficiently high alpha-particle energies a linear relation is approached for all crystals. No deviations from linearity were observed in plots of pulse height *vs* energy for deuterons or protons in crystals containing a Tl mole fraction of 0.0013. The fluorescent efficiency increases sharply with Tl concentration for mole fractions smaller than about 0.0015 and decreases for higher concentrations, this behavior being more pronounced for deuteron than for alpha-particle excitation. Four separate decay processes characterize the pulse shapes. In addition to the main

part of the pulse, which has a rise time (mean life) of about 5.9×10^{-8} sec and a long, concentration dependent, exponential decay (decay constant 2.3 to 3.5×10^{-7} sec, independent of exciting radiation), there are two faster decays: 1, an emission with a decay constant of 1.2×10^{-8} sec from crystals containing Tl mole fractions less than about 0.0002; and 2, a 1.5×10^{-8} sec decay from high Tl content crystals excited by particles having a large specific energy loss. The emission spectrum consists of two bands centered at about 3500 Å and 4100 Å, their exact positions depending upon the Tl concentration and shifting toward longer wavelengths with increasing Tl concentration. The 1.2×10^{-8} sec emission is from the short wavelength band, and the other emissions are from the band at 4100 Å. The dependence of the integrated pulse height on the Tl concentration and specific energy loss of the exciting particle are discussed, and possible explanations of the various decay processes are suggested.

I. INTRODUCTION

AN important factor in determining the fluorescent response of a thallium activated sodium iodide crystal, or more generally any activated alkali halide

phosphor, is the magnitude and uniformity of the activator concentration. There is often a considerable variation in the Tl concentration throughout a large

* This investigation was supported jointly by the U. S. Atomic Energy Commission and the Office of Naval Research.

† A preliminary report of some of the results was given at the

Washington meeting of the American Physical Society in May, 1953, *Phys. Rev.* **91**, 495 (1953).

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